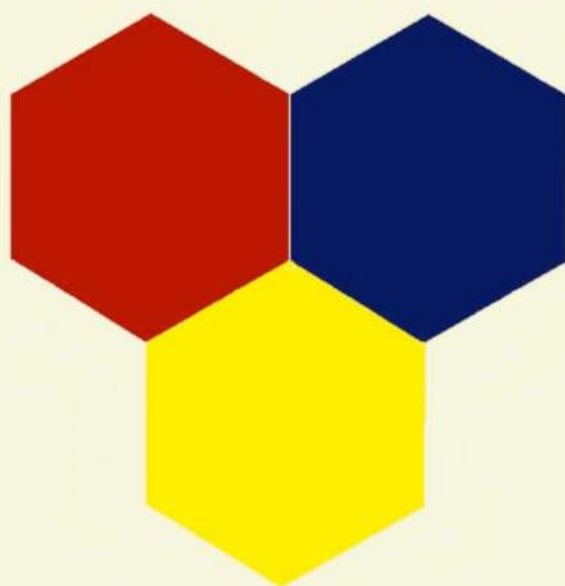


B. PAVLOV, A. TERENTYEV

ORGANIC CHEMISTRY



MIR PUBLISHERS • MOSCOW



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Boris BELITSKY

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Introduction

I. ORGANIC CHEMISTRY

1. Subject and Distinctive Features of Organic Chemistry. Early in the past century the term "organic chemistry" was applied to the chemistry of the substances that make up plant and animal organisms. The study of combustion processes by A. Lavoisier (1743-1794) had produced techniques for the ultimate analysis of these organic substances. This had revealed that the many different organic substances consisted of but a few elements, the most frequent among them being carbon, hydrogen, oxygen, and nitrogen.

From the simplest initial inorganic materials living organisms build up the most complex products: sugar, fat, cellulose, starch, protein substances, and the like.

The chemistry of those days had no means of preparing organic substances. This gave rise to the conviction that special laws held sway in living nature, due to the existence of a so-called "vital force" (*vis vitalis*) in living beings.

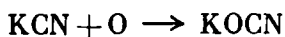
"In living nature the elements obey laws totally different from those ruling in inanimate material," wrote the famous Swedish chemist J. Berzelius in 1827. For this reason he defined organic chemistry as the "chemistry of vegetable and animal matter, or matter formed through the agency of a vital force".

In 1811 the St. Petersburg chemist Konstantin Kirkhgof (1764-1833) demonstrated that, when heated with a small amount of dilute sulphuric acid, large amounts of starch can be converted into sugar. By subjecting starch to the action of small amounts of malt, Kirkhgof obtained maltose. For such processes, in which chemical reactions proceed in the presence of minute amounts of certain substances that are not part of the reaction products, Berzelius proposed (1830) the term catalysis (derived from two Greek words "kata" meaning entirely and "lyo" meaning loose).

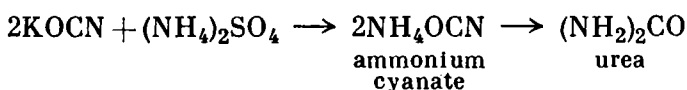
It was Berzelius's belief that the vital force operated in living nature by the catalytic power.

The vitalistic doctrine thus regarded organic chemistry as a distinct section of chemistry concerned with processes taking place under the influence of some specific and mysterious force defying comprehension. But by acting with various chemical reagents upon

organic substances of natural origin, chemists began to obtain numerous products not occurring in nature. These new artificial substances were, however, similar to natural substances in both composition and character. They, too, therefore, had to be called organic. It was in this way that organic chemistry based on synthesis arose and began to develop. In 1828 the German chemist F. Wöhler (a pupil of Berzelius's) succeeded in artificially preparing urea. His initial material in this experiment was an inorganic salt, potassium cyanide, which upon oxidation formed potassium cyanate



An exchange reaction between KOCN and ammonium sulphate then produces ammonium cyanate, which upon heating turns into urea:



By the middle of the past century a very great number of new substances of vegetable and animal origin had been isolated and studied. Even greater was the number of artificially obtained compounds not contained in living organisms. These syntheses and transformations were effected by ordinary chemical methods.

As a result of these achievements of synthetic organic chemistry, the vitalist theory lost ground and was completely abandoned. Nevertheless, the need to treat organic chemistry as a separate division of chemistry remained, although the reasons for this were now entirely different.

Early in the sixties there appeared two textbooks of organic chemistry: D. Mendeleev's *Organic Chemistry* (1860) and A. Butlerov's *An Introduction to a Comprehensive Study of Organic Chemistry* (1864-66). Roughly the same arguments were put forward in both these books in favour of viewing organic chemistry as a separate division of chemistry.

The complex compounds of carbon, whether of natural origin or synthetic, are distinguished by several specific features:

1. Organic compounds are less stable than inorganic compounds; they readily undergo changes upon heating and are combustible. These characteristics alone do not, however, permit us to draw a sharp dividing line between organic and inorganic compounds.

2. Carbon combines with hydrogen, oxygen, and nitrogen to form a very large number of substances. Carbon compounds are characterized by isomerism, which is very rare among inorganic compounds.

3. In organic chemistry there are series of substances similar in composition and chemical behaviour. These substances are known as homologues.

In this way the presence of carbon atoms in compounds distinguishes them from compounds not containing carbon. "The sum total of the above-mentioned properties and characteristics of organic compounds affords some possibility of distinguishing them from inorganic compounds" (Mendeleyev). Butlerov considered that for a substance to be listed as organic, it was enough for it to contain carbon: "All bodies containing carbon must then form the province of organic chemistry, or, to be more exact, the latter province should be termed the *chemistry of carbon compounds*. Without doubt, these compounds should be described in the general system of chemistry, but the wealth of relevant data, the specific chemical character, and the very importance of these substances furnish grounds for singling out the description of the carbon compounds to form a distinct section of science."

Mendeleyev defined the subject of organic chemistry with a certain qualification: "Organic chemistry is the section of chemistry concerned with the study of the properties and changes (reactions) of the impermanent carbon compounds."

Later, after Butlerov had founded the theory of chemical structure, C. Schorlemmer defined organic chemistry as the "chemistry of the hydrocarbons and their derivatives". By so doing, he sought to accentuate the following points: (a) the ability of carbon to form C—C atom chains; (b) the presence of hydrogen in most organic molecules, and (c) the possibility of hydrogen being replaced by various other atoms (the halogens, O, S, N, P...).

This definition is undoubtedly correct and serves to bring out clearly the distinctive features of the vast number of organic substances of relatively simple structure, which at that time (1880) accounted for the bulk of the synthesized organic compounds. Such a definition forms the basis for the classification of organic compounds according to genesis: every complicated compound is regarded as having been formed from some hydrocarbon by the replacement of hydrogen atoms by heteroatoms and various functional groups. Schorlemmer's definition becomes too narrow, however, for the more complex compounds with a high relative number of non-carbon atoms (silicon, nitrogen, oxygen...). In these cases Butlerov's and Mendeleyev's definitions appear more correct.

Organic chemistry thus forms a distinct province of the science of chemistry. The physical and chemical properties of organic substances and their structure are determined by the carbon atoms they contain.

Nowadays we can put our finger more exactly on the specific properties of carbon as an element and examine from contemporary positions what distinguishes typical carbon compounds from the compounds of other elements. These distinguishing features are as follows:

1. Carbon occupies a position in the Periodic System midway between the typical metals and non-metals. It has the same valency of 4 in terms of hydrogen and oxygen. It is thus a *tetravalent element* in nearly all its compounds.

2. Carbon combines with most elements. Especially characteristic of carbon is its ability to form complicated and stable molecules, in which the carbon atoms are linked in *continuous chains*: linear, branched, or of complex ring structure. The bonds between these atoms can be single (ordinary), double, or triple.

3. In typical chemical reactions in mild conditions, these carbon bonds, which form something like a "carbon skeleton" of the molecule, are seldom disrupted. The reactions of decomposition or synthesis usually proceed in such a manner that bond rupture or the formation of new bonds is not accompanied by the breakdown of the rest of the linkages in the molecules participating in the reaction (*principle of least change*).

4. Owing to this ability to form complicated molecules consisting of diversely linked atoms, molecules of one and the same composition may differ in structure and, consequently, in properties. This phenomenon called *isomerism* is a most typical feature of carbon compounds.

5. Carbon does not tend to form ionic compounds of the salt type. Even aqueous solutions of organic compounds are seldom electrolytes (i.e., do not conduct electricity). Bonds in organic molecules are, as a rule, covalent.

6. The vast majority of organic compounds contain hydrogen. The C—H bond is hardly ever ionic. The hydrogen atoms linked to carbon are usually less reactive than those connected with oxygen (O—H), nitrogen (N—H), or other elements. The hydrocarbon part of the molecule is usually more inert than the groups containing heteroatoms (O, N, S, P...). The chemical character of complicated organic compounds is therefore determined by the presence of "*functional*" groups containing heteroatoms.

2. Organic Chemistry and the Organic Synthesis Industry. Organic chemistry, which arose as the science of the composition and transformations of the products of living nature, subsequently began to develop along the lines of the artificial preparation of carbon-containing substances. Along these lines it has made great strides, both theoretical and practical.

Most of the natural organic substances being complicated compounds, their study was beyond the reach of the young science. Its first successes were therefore in investigating simpler substances, such as ethyl alcohol, acetic acid, and benzene, from which it was possible to derive a multitude of new compounds not encountered in living nature. So it was that from a science concerned with sub-

stances of organic origin, organic chemistry turned into a science dealing with substances obtained by synthesis.

What are the forces behind the progress of this science? How, why, and in what direction are the various fields of organic chemistry developing?

The history of organic chemistry is bound up closely with the history of human society and with the appearance of new requirements and the birth of new industries. The alcohols and acetic acid are products of the food industry. The study of fermentation and the utilization of the products of that industry provided chemists with readily available material for preparing a host of useful substances artificially. The fat and soap industry stimulated the chemistry of organic compounds of the "fatty"* division.

The widespread industrial use of the dry distillation of coal for the manufacture of illuminating gas and of coke led to a study of the basic products (gases) and by-products of that industry. As early as 1825 M. Faraday discovered benzene by isolating it from the liquid that condensed in gas mains. Chemists had to take up the problem of utilizing large amounts of coal-tar, and its distillation yielded many "aromatic" hydrocarbons besides benzene: toluene, naphthalene, anthracene, a number of phenols, and many other products. The chemical treatment of the tar produced nitrogen compounds, amines, and many other compounds, which found application as artificial dye-stuffs ("aniline" dyes), explosives, etc. There arose big industrial establishments utilizing coal products.

The urgent practical problems posed by industrial development required profound theoretical research. "There is nothing more practical than a good theory." This well-known adage fully applied to organic chemistry.

Several generations of chemists had to make tremendous efforts to build up a theory of chemical structure. This theory became a sound foundation for gaining an insight into chemical processes, for planned synthesis, for predicting the properties of substances not yet synthesized, and for foreseeing their practical applications.

Theoretical progress in this or that field of organic chemistry has been most intimately associated with practical requirements. For example, research in the hydrocarbons and, especially, in organic catalysis has been largely connected with problems posed by the motor fuel industry. The discovery of valuable new dyes and drugs similarly gave a powerful impetus to the chemistry of heterocyclic compounds. Such chemical industries as the manufacture of artificial fibre, synthetic rubber, and plastics, to name only a few, arose

* Compounds of acyclic structure are often referred to as aliphatic, from the Greek word *aleiphar* meaning oil or fat.

and attained a high degree of development in the past 40-50 years, the chemistry of high-molecular organic compounds developing in step with them.

Just as the future building or mechanical engineer, before undertaking building work, has to study the properties of building materials and the fundamentals of mechanics, so the chemist—the builder of the chemical molecules of organic substances—first has to learn, by simple examples, the properties of organic compounds and the laws governing their chemical transformations.

II. WORKING WITH ORGANIC SUBSTANCES

3. Isolation and Purification of Organic Substances. To analyze and study an organic substance it is necessary to obtain it in pure form. The principal techniques of purifying and isolating

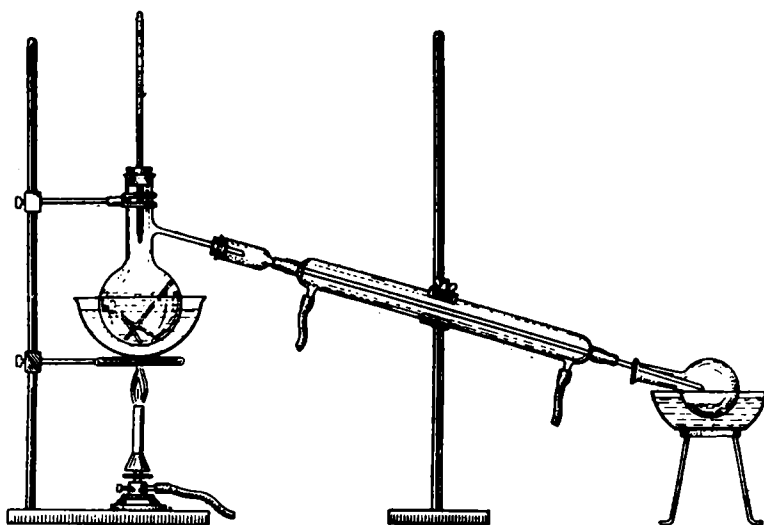


Fig. 1. Distillation apparatus.

organic compounds from substances occurring in nature or from reaction products are: distillation, extraction by solvents, crystallization, and filtration.

Distillation is the most widespread method of purifying organic substances.

When a liquid is to be distilled, it is poured into a round-bottom distillation flask with a side tube (Fig. 1); the thermometer is adjusted so that its bulb is just below the side tube, and cold water is made to flow through the jacket of the condenser upwards (counter-flow principle). Pieces of glass capillary tubing, sealed at the upper end, are put in the flask with the liquid. The presence of the

air in the capillaries facilitates the formation of steam, and boiling proceeds smoothly, without what is known as bumping. Pieces of unbaked clay (plates) or other porous material may be used instead of capillary tubing.

Mixtures of substances with substantially different boiling points can be separated by distillation, this yielding the component parts of the mixture in sufficiently pure form.

When distilling a mixture of substances whose boiling points are near to one another, it is expedient to use dephlegmators or fractionating columns. The simplest fractionating columns are glass tubes filled with glass beads or short metal spirals. At the present time there are fractionating columns that make it possible to separate mixtures of liquids with boiling points differing by as little as 1-2 degrees.

Some substances decompose when distilled under ordinary conditions. To avoid decomposition they are distilled at reduced pressure. The lower the pressure, the lower the boiling point of a substance. When the pressure is reduced, for example, from 760 to 10-15 mm Hg (such a vacuum can be obtained by a suction pump), the boiling point sinks by about 100° ; when the pressure is lowered to tenths or hundredths of a millimetre (a so-called high vacuum, obtained by oil or mercury pumps), the boiling point drops by 200° .

A specific type of distillation at reduced pressure is *molecular distillation*. This is conducted at pressures of not more than 0.001 mm Hg. The apparatus used (Fig. 2) is such that the molecules of the vaporized substance do not return and do not encounter any molecules of air, thanks to the very short distance between the heated and the cooled surface. This makes it possible to distil substances such as nitroglycerine (p. 165) and some sugars.

Substances with a low solubility in water and an appreciable vapour tension at about 100° may be isolated by distillation with steam. The steam required is, as a rule, generated in a separate steam boiler and introduced by tube into the round-bottom flask with the mixture containing the substance to be isolated, the mixture of vapours is condensed in the condenser and collected in the receiver. The apparatus for steam distillation is shown in Fig. 3. Many substances can be isolated from mixtures and purified by steam distillation.

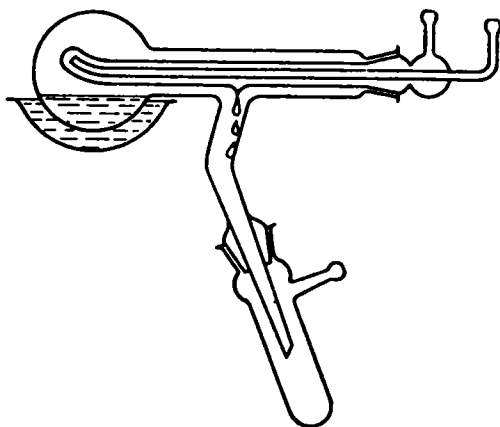


Fig. 2. Apparatus for molecular distillation.

Distillation is practised extensively in many chemical industries. At alcohol plants, for instance, fermentation produces a mixture of alcohols, from which ethyl alcohol is separated in rectification columns. The remaining mixture of "fusel oil" is subjected to further fractionation, which yields propyl, isobutyl, and isoamyl alcohols. Petroleum distillation at refineries produces various petrol fractions and less volatile cuts: ligroin, paraffin oil, diesel oil, etc.

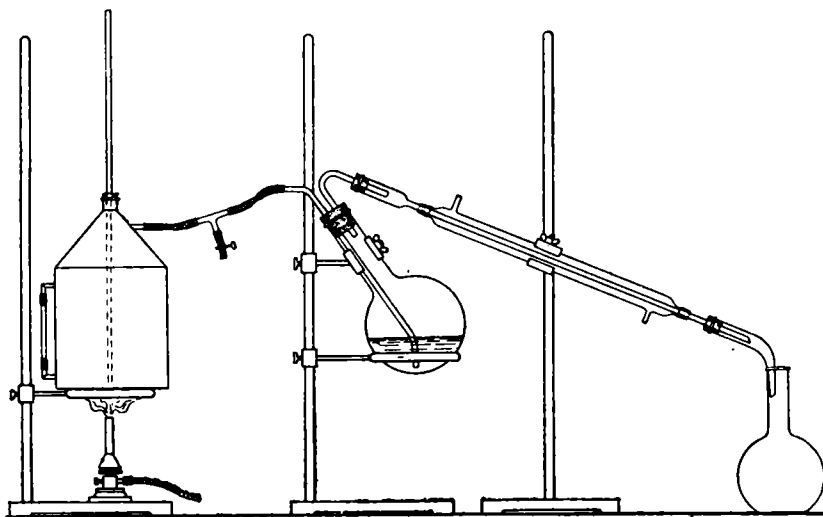


Fig. 3. Steam distillation apparatus.

Extraction from an aqueous solution by volatile solvents immiscible with water (ether, petroleum ether, chloroform, carbon disulphide, etc.) is a widespread method of isolating substances both in the laboratory and in industry. The technique is used to isolate essential oils and alkaloids from plants, various antibiotics from moulds, etc. In the laboratory the following procedure is employed. The aqueous solution of the substance is poured into a separating funnel; a solvent, such as ether, is added; the funnel is shut with a glass stopper and shaken vigorously. In the process the substance is partly extracted from the water by the ether. The contents of the funnel are then allowed to settle, with the result that two layers are formed. The stopper is now removed, and the lower (aqueous) layer is run off through the tap; the upper layer (ether extract) is poured out through the top of the funnel. The aqueous solution may then be treated with ether again. Provided the substance is readily soluble in ether and poorly soluble in water, a repetition of the operation several times extracts it from the solution almost completely. The ether extracts are combined and dried, with the addition of potash, potassium hydroxide, fused calcium chloride, or sodium or magnesium sulphate dehydrated by calcination. The dried solution is

filtered and then placed in a boiling water bath to remove the ether. The residue is further purified by distillation or crystallization.

Solid substances are extracted in the Soxhlet apparatus (Fig. 4).

A technique that is finding steadily wider application is extraction with two solvents, which makes it possible to separate complex mixtures of organic substances with similar properties. The apparatus used for this purpose usually operates automatically.

Crystallization and Filtration. When a hot solution containing a mixture of two

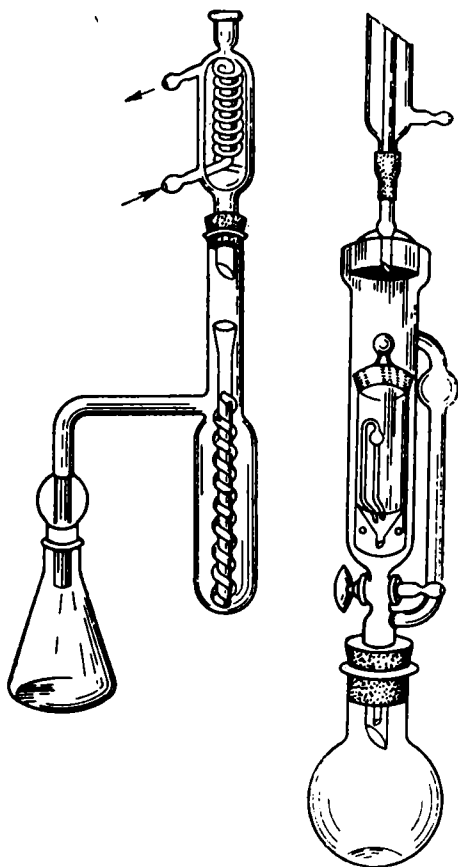


Fig. 4. Devices for continuous and batch extractions of solid substances at the boiling point of a solvent.

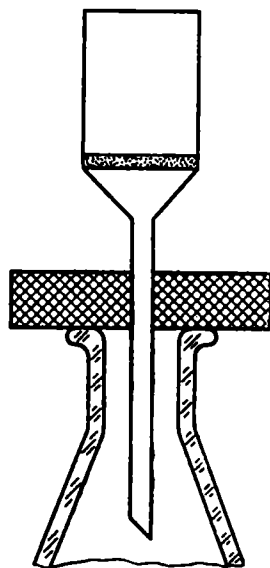


Fig. 5. Connection of a funnel with a suction flask.

or more solid substances is cooled, the substance in respect to which the solution at a given temperature is supersaturated begins to crystallize. The crystals formed may be filtered off. Filtration is often accomplished in the laboratory by means of a glass or porcelain funnel with a flat, perforated partition, on which a circular filter paper is placed. The funnel is inserted in a cork and fitted into a filter flask (Fig. 5). The flask is attached to a suction pump, which removes air. This reduces pressure in the flask and speeds filtration. Centrifuges and ultracentrifuges are used today to separate precipitates, especially in working with colloids and finely divided precipitates.

4. Determination of Physical Constants. Every pure substance has definite physical constants. These may serve as a means of identifying the substance. At the same time the constancy of this or that physical characteristic in repeated purification runs may often indicate that the substance is in a pure state.

The physical constants determined most frequently in organic substances are the melting point and boiling point, the relative density, and the index of refraction.

Melting Point. To determine the melting point of a substance, it is carefully ground to a powder and put into a capillary tube 1-1.5 mm in diameter sealed at one end; the layer of powder should be about 2 mm high. The tube is attached (e.g., by a drop of sulphuric acid) to a thermometer so that the substance is close to its bulb. By means of a stopper with an air vent the thermometer is then placed in a flask (Fig. 6) three-quarters filled with concentrated sulphuric acid. The apparatus is heated slowly, and the temperature at which the substance melts is noted. If the substance contains no admixtures, melting takes place within a small temperature range ($0.5-1^{\circ}$). Even small admixtures appreciably lower the melting point of a substance; moreover, melting in that case is not sharply defined and extends over a considerable temperature range. Changes in atmospheric pressure do not have a noticeable effect on the melting point.

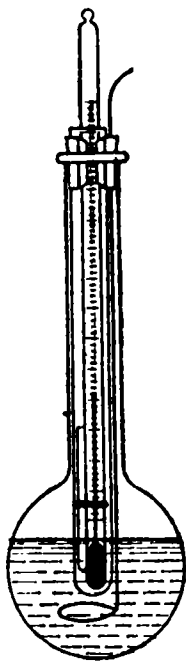


Fig. 6. Arrangement for determining melting point.

Boiling Point. When a substance is purified by distillation, its boiling point is determined at the same time. If we have a mixture of liquids, the boiling point will in most cases rise continuously during distillation. But if a pure substance is being distilled, the thermometer will show the same temperature throughout. A change in atmospheric pressure affects the boiling point of a substance appreciably (sometimes by as much as $2-3^{\circ}$). For this reason it is necessary to indicate the pressure at which distillation was carried out; the absence of such an indication is taken to mean that the determination was made at normal atmospheric pressure (760 mm Hg).

To determine the boiling point of a substance by the Sivolobov method, all we need to have is one drop of the liquid. The liquid is put in a very narrow tube about 2 mm in diameter, sealed at the bottom. A thin capillary tube, sealed at the top, is lowered into it. The tube with the liquid is attached to the thermometer of

a set-up for melting point determination, as shown in Fig. 7, after which the flask is slowly heated. A continuous stream of tiny bubbles, issuing from the capillary tube, will indicate that the liquid has begun to boil. Heating is then discontinued and the temperature noted at which the bubbles abruptly cease. This is the liquid's boiling point.

Density and Relative Density. Liquids are conveniently characterized by their density. This is often determined in the laboratory and in industry by means of the areometer and the alcoholimeter. Relative density may be determined by means of a 1-5 ml pycnometer (Fig. 8). First, it is necessary to determine the weight of the water that the pycnometer holds. This is done by filling the pycnometer, after it has been weighed, with distilled water and placing it for 20-30 minutes into a vessel with water at a temperature of 20°. The pycnometer is then wiped with filter paper and weighed. The weight of the liquid in the pycnometer is determined in the same way.

The relative density at 20° (d_{20}^{20}) is the ratio of the determined weight of the liquid to the weight of an equal volume of water. It is customary to make this comparison with the density of water at 4°, which is approximately equal to 1 g/cu cm. Since the density of water at 20° is 0.9983, the relative density (d_4^{20}) may be found according to the formula:

$$d_4^{20} = \frac{m}{w} \times 0.9983,$$

where m = weight of the substance in the volume of the pycnometer at 20°

w = weight of an equal volume of water at the same temperature, and

0.9983 = relative density of water at 20°.

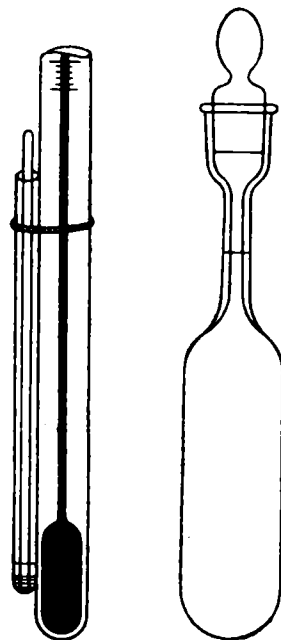


Fig. 7. Thermometer with tube and capillary.

Fig. 8. Pycnometer.

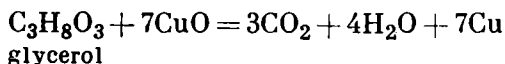
5. Composition of Organic Substances. Qualitative Analysis. Apart from carbon, organic substances most frequently contain hydrogen, oxygen, and nitrogen. These four elements are referred to as *organogens*. Besides them, the molecule of an organic substance may also contain other elements.

Many protein substances contain sulphur; the casein of milk contains phosphorus; the haemoglobin of the blood contains iron,

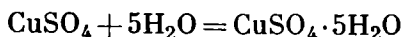
and chlorophyll contains magnesium. Highly important in various syntheses are organic substances containing halogens.

A very interesting and distinct group are the so-called *organoelement compounds*, whose molecules contain atoms of diverse elements, such as metals, linked directly to carbon.

Detection of Carbon and Hydrogen. The presence of carbon in many organic compounds may be determined by the charring of the substance upon careful heating. A more general test for carbon, and for hydrogen simultaneously, consists in heating the organic substance, mixed with an oxidizing agent, in a test-tube; the oxidizing agent used is fine copper oxide powder. The carbon of the organic substance is oxidized to carbon dioxide, while the hydrogen is oxidized to water, e.g.:



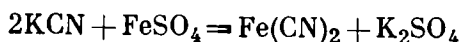
The gas evolved is passed through a test-tube with a freshly prepared solution of lime-water. The presence of carbon dioxide is confirmed by the formation of a white precipitate of insoluble calcium carbonate CaCO_3 . Water may be detected in the combustion products by passing the gas into a dry test-tube with some anhydrous powdered copper sulphate CuSO_4 at the bottom (it is obtained as a white powder by the calcination of blue vitriol crystals). The anhydrous copper sulphate avidly absorbs water, returning to the crystalline blue vitriol state:



Detection of Nitrogen. To detect nitrogen, a small quantity of the organic substance is heated strongly with metallic potassium or sodium. The potassium (or sodium) combines with part of the carbon and nitrogen of the organic substance, forming potassium cyanide KCN (or sodium cyanide NaCN). The resulting melt is dissolved in water, with the addition of a solution of a ferrous salt, such as iron vitriol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and a solution of ferric chloride FeCl_3 , in which iron is trivalent. When acid is added, a dark blue precipitate of Prussian blue is formed.

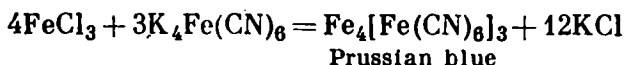
Prussian blue is formed by virtue of the following reactions.

At first there is a double decomposition reaction between potassium cyanide and iron vitriol, resulting in the formation of ferrocyanide $\text{Fe}(\text{CN})_2$ and potassium sulphate K_2SO_4 :



The ferrocyanide reacts with the remainder of the potassium cyanide, forming potassium ferrocyanide $\text{K}_4\text{Fe}(\text{CN})_6$. This reacts

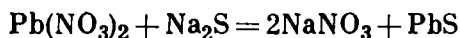
with ferric chloride, producing Prussian blue, a compound of blue colour:



If the substance contains a great deal of nitrogen, the Prussian blue forms a precipitate; if there is little nitrogen, the solution acquires a greenish-blue hue.

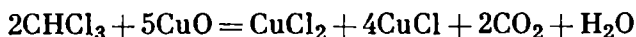
Detection of Sulphur. To detect sulphur, the organic substance is heated with metallic sodium, just as in testing for nitrogen. The sodium combines with the sulphur, forming sodium sulphide. The melt is then dissolved in water, and a solution of either lead nitrate $\text{Pb}(\text{NO}_3)_2$ or of sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ is added.

Lead nitrate reacts with the sodium sulphide, forming lead sulphide PbS , a black precipitate:



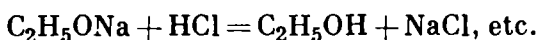
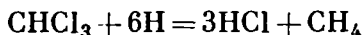
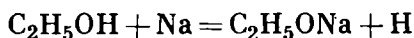
Sodium nitroprusside, reacting with sodium sulphide, produces a deep violet colour.

Detection of Halogens. The Beilstein test for halogens is the simplest. The organic substance is heated in a flame with copper oxide. The oxygen of the copper oxide oxidizes the carbon and the hydrogen of the organic substance to carbon dioxide and water, while the copper combines with the halogen. With chloroform CHCl_3 , for instance, the reaction may be expressed by the equation:

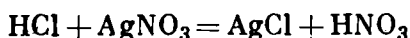


The resulting copper halide, being volatilized in the flame, gives a green coloration. This is proof that the organic substance contains a halogen.

In the Stepanov method for the detection of a halogen, a solution of the substance in alcohol is heated with metallic sodium. The sodium displaces hydrogen from the hydroxyl of the alcohol, and the nascent hydrogen detaches a halogen atom, transferring it into the ionic state:



When the reaction ends, the solution is diluted with water and acidified with some nitric acid, after which a solution of silver nitrate is added. This produces a characteristic flaky precipitate of silver halide salt:



Determination of the Presence of Oxygen. The detection of carbon, hydrogen, nitrogen, sulphur, and the halogens does not present any difficulties. The detection of oxygen, however, is much more difficult, and its presence is in most cases determined from quantitative analysis data.

For example, if by quantitative analysis it is found that a substance consists of 58.5% carbon, 4.1% hydrogen, and 11.4% nitrogen, and if, furthermore, no other elements are detected, the remainder is attributed to oxygen.

In this example

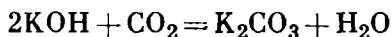
$$58.5 + 4.1 + 11.4 = 74\%$$

i.e., the substance contains $100 - 74 = 26\%$ oxygen.

To detect the individual elements of an organic compound it is thus necessary, first, to decompose it by complete burning, or oxidation, or fusing with metallic sodium, in order to turn the carbon, hydrogen, nitrogen, and other elements into simple substances convenient for qualitative determination.

6. Quantitative Analysis. Determining the quantitative content of individual elements in organic substances is called elementary analysis. The principal organogens C, H, N, and O are usually estimated by burning a weighed quantity of the substance in a tube of refractory glass or quartz. In macroanalysis it is customary to burn a quantity weighing 0.15-2 g; in microanalysis, 2-5 mg. Microdeterminations make it possible not only to operate with much smaller quantities, but also to perform the analysis much faster. The apparatus for elementary analysis, as well as the computation procedure, is described in manuals of practical work in organic chemistry; we shall, therefore, confine ourselves here to the principles followed in estimating the various elements.

Estimation of Carbon and Hydrogen. An accurately weighed quantity of the organic substance is heated with copper oxide in a current of oxygen, this producing carbon dioxide and water. The water is absorbed in a U-tube filled with calcium chloride or magnesium perchlorate $\text{Mg}(\text{ClO}_4)_2$, called anhydron, which combines avidly with water. The carbon dioxide is absorbed in a potash bulb by a concentrated solution of potassium hydroxide, which reacts with the carbon dioxide according to the following equation:

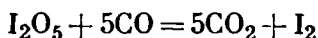


By weighing the U-tube before and after the experiment, we establish the amount of water formed; similarly, the increase in the weight of the potash bulb indicates the amount of carbon dioxide. These data make it possible to calculate the percentages of carbon and hydrogen in the substance.

Estimation of Nitrogen. Nitrogen in an organic compound may be estimated by several methods. In the Dumas method a known weight of the substance is burned with copper oxide in a tube in a current of carbon dioxide. Elementary nitrogen (N_2) is evolved and is, with the other oxidation products (H_2O and CO_2), expelled into a nitrometer filled with a concentrated potassium hydroxide solution, which absorbs carbon dioxide and the condensed water. The collected nitrogen is measured by volume.

The Kjeldahl method is employed frequently. Here the known weight of the substance is boiled with concentrated sulphuric acid, which chars and then burns up the substance, while the acid is partly converted into SO_2 . The nitrogen is turned into ammonium sulphate. When oxidation is over, the solution is made alkaline. The evolved ammonia is absorbed by a hydrochloric or sulphuric acid solution of known concentration.

Estimation of Oxygen. As stated above, oxygen is usually estimated "by difference". Methods of "direct" estimation have, however, also been proposed. In M. Korshun's method the known weight of the substance is heated in a quartz tube in a current of nitrogen. The decomposition products are passed over very hot coal, which turns all the oxygen into carbon monoxide. This is estimated quantitatively by means of iodine pentoxide. The estimation is based on the reduction of the iodine pentoxide, heated to 150° , by the carbon monoxide:



The iodine is estimated by titration with thiosulphate.

Estimation of Halogens and Sulphur. A known weight of the substance is heated in a sealed thick glass tube with nitric acid (relative density = 1.5) in the presence of silver nitrate. The nitric acid oxidizes the carbon and the hydrogen of the organic substance to carbon dioxide and water, while the halogen forms a precipitate of low solubility ($AgCl$, $AgBr$, AgI). The precipitate is filtered, washed, dried, and weighed.

Sulphur is estimated by an analogous procedure, with the sole difference that no silver nitrate is added. As the oxidation of sulphur is facilitated by the presence of bromine, a few crystals of pure potassium bromide are often added to the weighed quantity of the substance. The nitric acid oxidizes the sulphur to sulphuric acid which is precipitated by a solution of barium chloride as barium sulphate. The precipitate is filtered, washed, calcined at 500° , and weighed. This method of halogen and sulphur estimation was proposed by Carius.

7. Derivation of Empirical Formulas. Quantitative analysis tells us the composition of a substance in percentages. By what pro-

cedure, knowing the percentage of each element in a substance, can we express its composition not in percentages, but in atomic units, i.e., how can we derive its chemical formula?

Supposing we find by analysis that the substance contains 79.20% carbon; 15.07% oxygen, and 5.73% hydrogen, i.e., that the relative proportions of carbon, oxygen, and hydrogen are: 79.20 : 15.07 : 5.73.

To derive the empirical formula of the substance we must know the ratio of the numbers showing how many atoms of the various elements make up a molecule. To obtain this ratio the numbers expressing the percentages of the elements must be divided by their atomic weights, since the higher the atomic weight of an element, the fewer atoms correspond to the found percentage. Since the atomic weight of carbon is 12, of oxygen 16, and of hydrogen 1.01 (approximately), we get:

$$\frac{79.20}{12} = 6.6 \quad \frac{15.07}{16} = 0.942 \quad \frac{5.73}{1.01} = 5.67$$

i.e., for 0.942 atoms of oxygen there are 5.67 atoms of hydrogen and 6.6 atoms of carbon. But a molecule of a substance cannot contain fractions of atoms. We therefore have to find out how many atoms of carbon and hydrogen there are not for 0.942 atoms, but for 1 atom of oxygen. This is done by dividing our numbers by 0.942 *:

$$\frac{6.6}{0.942} = 7 \text{ (number of carbon atoms)}$$

$$\frac{5.67}{0.942} = 6 \text{ (number of hydrogen atoms)}$$

$$\frac{0.942}{0.942} = 1 \text{ (number of oxygen atoms)}$$

Consequently, for 1 atom of oxygen in the molecule of the substance there are 7 atoms of carbon and 6 atoms of hydrogen. The composition of the substance may therefore be expressed by the formula C_7H_6O .

8. Molecular Weight Determination. We have established that a molecule of our substance contains 7 atoms of carbon and 6 atoms of hydrogen for every atom of oxygen, i.e., that its composition may be expressed by the formula C_7H_6O . But the molecules of the substances $C_{14}H_{12}O_2$, $C_{21}H_{18}O_3$, $C_{28}H_{24}O_4$, etc., likewise contain 6 atoms of hydrogen and 7 atoms of carbon for every atom of oxygen; the composition of these substances is expressed by the same percentages. Hence, the formula C_7H_6O is not the only one possible

* It is necessary to divide by the smallest of the numbers indicating atom contents. In the given example such a number is that indicating the number of oxygen atoms.

for our substance; it is merely the simplest. To establish which of these formulas is the true one we must determine the molecular weight of the substance. Since the atomic weight of carbon is 12, oxygen 16, and hydrogen 1, the molecular weight of the substance corresponding to the formula C_7H_6O is 106 ($12 \times 7 + 6 + 16$), the molecular weight of the substance corresponding to the formula $C_{14}H_{12}O_2$ is 212, etc.

In accordance with Avogadro's Law, the molecular weight equals twice the gas (or vapour) density in terms of hydrogen: $M = 2d$.

In our example, if the density in terms of hydrogen is 53, the molecular weight of the substance is 106 and its formula is C_7H_6O ; if the vapour density in terms of hydrogen turns out to be 106, the molecular weight is equal to 212 and the formula of the substance is $C_{14}H_{12}O_2$, etc.

If the substance is not vaporizable, the molecular weight is determined by the elevation of the boiling point or the depression of the freezing point of a solution of the substance in some solvent.

Elementary analysis and molecular weight determination thus make it possible to establish merely a general "molecular" formula. For most of the typical inorganic substances chemical analysis ends at that. But in organic chemistry one and the same molecular formula nearly always corresponds to many substances differing in physical and chemical properties (isomers). The molecules of these substances differ in their atomic linkages: they have a different "chemical structure". What chemical structure is and what methods are used for determining it we shall learn in the next chapter.

III. THEORY OF CHEMICAL STRUCTURE

9. Theory of Radicals and Theory of Types. In 1861 Professor Alexander Butlerov of the University of Kazan for the first time propounded the basic ideas of a theory of the chemical structure of organic compounds. To assess the significance of the structural theory founded by A. Butlerov, we must form a picture of the theoretical concepts that prevailed in organic chemistry in the period that led up to the appearance of his theory.

One of the first theories of organic chemistry was Berzelius's theory of *electrochemical dualism* (1820-40). Berzelius identified the cause of chemical affinity as the attraction of particles with opposite electric charges. He believed molecules of complex substances to consist of two oppositely charged parts. This belief arose from observations of the electrolysis of salts, acids, and bases. Oxygen was considered to be the most electronegative element; the atoms of the alkaline metals, the most positive. Sulphur combined with

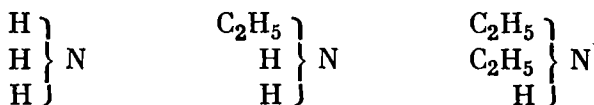
oxygen to form sulphur trioxide SO_3 , a molecule with a predominant negative charge. The oxides of the metals sodium and potassium, on the other hand, had a surplus electropositive charge. Therefore, it was reasoned, the molecule of sodium sulphate could be represented thus: $(\text{Na}_2\text{O})^{(+)} \cdot (\text{SO}_3)^{(-)}$. The passage of a direct electric current through a solution of this salt, it was further thought, decomposed the substance into the initial alkali and sulphuric acid. Since the Na_2O particle was positively charged, it was attracted to the negatively charged cathode, while the $(\text{SO}_3)^{(-)}$ was drawn to the anode.

Most organic compounds do not conduct electricity in solutions. Attempts to explain their structure from the standpoint of electrochemical dualism therefore ran up against great difficulties. Nevertheless, Berzelius doggedly maintained that every organic compound, like inorganic salts, consisted of two *compound radicals* of opposite electric charge. Such compound organic radicals could exist in the free state, just as calcium oxide CaO and sulphur trioxide SO_3 .

Finding, studying, and isolating such compound radicals appeared to be one of the major scientific tasks facing organic chemistry.

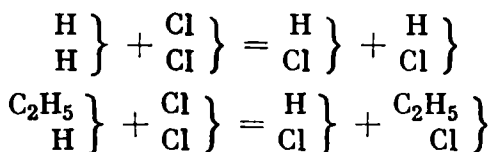
But as the study of organic compounds proceeded, more and more observations failed to fit in with this theory. Finally, the theory of radicals gave way to the *unitary theory* of Gerhardt*-Laurent (or *theory of types*, 1840-60). The molecule of an organic compound, according to this new theory, did not consist of distinct oppositely charged parts, but was a single whole. In reactions of double decomposition, the most typical reactions of organic compounds, the molecules were believed to break up into *residues*, which arose in the course of the reaction, but had not existed in the initial molecules and were incapable of existing in the free state. According to their characteristic reactions, all organic compounds were referred to several types.

All the amines resulting from the action of ammonia upon the halogen derivatives of organic compounds thus formed the compound ammonia type:



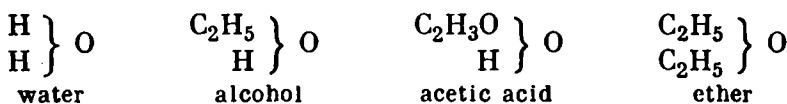
* Charles Gerhardt, French chemist (1816-56). He was born and worked in Strasbourg. With Auguste Laurent (1807-53), he founded the unitary theory, the theory of chemical types, and an original classification of organic compounds. His experimental work included the preparation of mixed anhydrides of acids and the preparation of substituted amides (formanilide, acetanilide, benzanilide, etc.) and sulphonamides.

Reactions between the hydrocarbons and chlorine follow the same pattern as the interaction of hydrogen with chlorine:

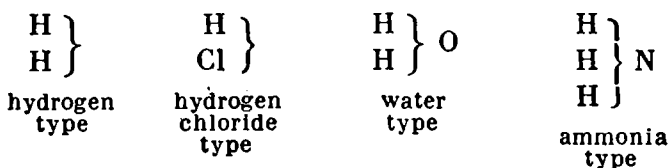


Therefore the hydrocarbons were referred to the hydrogen type, while the halogen derivatives were referred to the hydrogen chloride type.

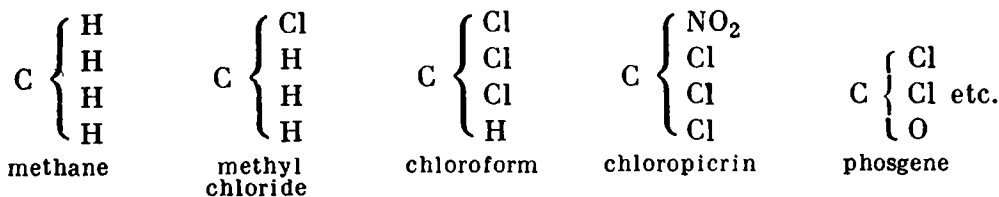
The alcohols, acids, and ethers were regarded as derivatives of water, in which one or two atoms of hydrogen had been replaced by organic residues:



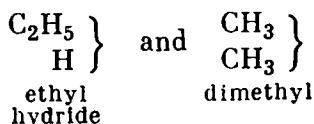
The following were thus chosen as the fundamental types of organic compounds:



In 1858 A. Kekulé proposed still another type, the methane type, embracing the compounds:



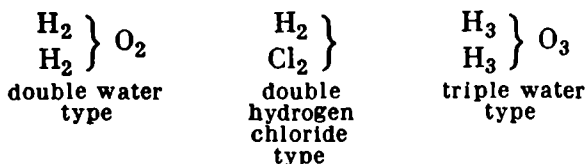
Obviously, the hydrocarbons could also be referred to the methane type. It is interesting to note that as far back as the early sixties the opinion prevailed among chemists that the compound C_2H_6 existed in the form of two isomeric compounds:



In this way it was at first assumed that organic compounds were analogous in their properties to inorganic compounds, i.e., to compounds actually in existence. Soon, however, chemists discovered organic compounds whose properties were such that they did not

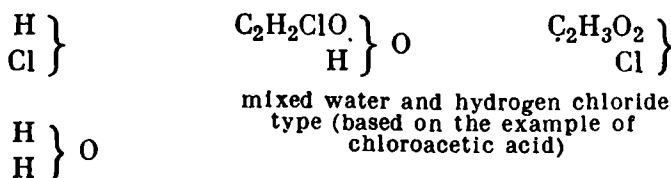
fit into these simple types. One such compound was glycerol, whose molecule contains three OH water residues instead of one. Similarly, a molecule of glycol contains two such residues. The diamines appeared to consist of two conjugated molecules of ammonia.

It had to be assumed that there existed "*multiple types*":

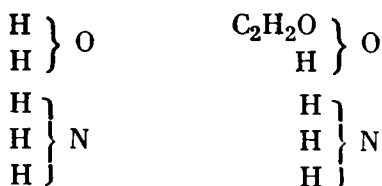


This amounted to recognition of the actual existence of organic compounds corresponding to double water, double hydrogen chloride, etc., that is, to inorganic compounds which do not exist in reality.

New and more complicated organic compounds were found, which had to be referred to two different types. There was, for instance, chloroacetic acid, which reacted according to both the water type and the hydrogen chloride type. This gave rise to the theory of "*mixed types*":



The action of ammonia upon chloroacetic acid produces aminoacetic acid, which has to be referred to the mixed water-ammonia type:



There are no inorganic prototypes of these compounds in existence; the mixed water and hydrogen chloride type is not an aqueous solution of hydrogen chloride (i.e., ordinary hydrochloric acid). Nor are the properties of aminoacetic acid like those of an aqueous solution of ammonia. But if the original types do not really exist, do the typical formulas of organic compounds necessarily reflect the actual structure of their molecules?

Gerhardt and his followers answered this question in the negative. The typical formulas were merely rational formulas, indicating a certain general analogy in chemical transformations. Since there could be many such transformations, one and the same compound

could have several such formulas. By studying chemical properties it was impossible, in the view of Gerhardt and his followers, to determine the real structure of a molecule of a substance.

Such a conclusion, leading to philosophical agnosticism, was all the more strange because the theory of types had done a very great deal in the course of its development to enrich chemistry factually.

Indeed, by the sixties the basic premises for a correct theory were actually on hand. Chemists had begun operating with true atomic weights, instead of the former equivalents; the concept of the valency of elements, instead of the former equivalents; the concept of the valency of elements had been established. Further highly important work for founding a new theory of organic chemistry was done in 1858-60 by the Scottish scientist Archibald Scott Couper and the foremost German chemist August Kekulé. They established that carbon has a constant valency in all its compounds, proposed a new type of organic compounds, the methane type (Kekulé, 1858), and demonstrated the ability of carbon to form chains. However, these isolated facts and observations were not brought together into a single consistent theoretical system. It was left to Alexander Butlerov* to found this new theory.

10. Butlerov's Theory of Chemical Structure. The basic ideas of the new theory were first made public by Butlerov in a paper which

* Alexander Butlerov (1828-1886) was born in the town of Chistopol, Kazan Province. He began taking an interest in chemistry while still at school and became especially interested in the subject at college. It was as a student at the University of Kazan, under Professor N. Zinin, that he did his initial research. In 1847 Zinin left for St. Petersburg, and Butlerov began working under K. Klaus, whose interests were not confined to chemistry (he discovered the element ruthenium), but extended to the natural sciences generally, in which he was well versed. Butlerov's first scientific paper was on a subject unrelated to chemistry. It was entitled *Day-Flying Moths of the Volga-Don Fauna*. His M.Sc. dissertation was, however, on a chemical subject: "Concerning the Oxidizing Effect of Osmic Acid on Organic Substances" (1851).

In 1852 Butlerov took over from Klaus on the latter's retirement and became a professor of Kazan University. His D.Sc. dissertation, "On Essential Oils", was presented at Moscow University. In 1857-58 Butlerov was sent abroad to become acquainted with some of the chemical laboratories in Germany and France. At Wurtz's laboratory he carried out an investigation involving the preparation and chemical study of methylene iodide CH_2I_2 . He continued this investigation later at the laboratory in Kazan. Butlerov proved that the product of the action of copper upon methylene iodide is not the free methylene radical CH_2 , but the hydrocarbon ethylene C_2H_4 . From methylene iodide he also prepared a polymer of formaldehyde (dioxymethylene); the latter, when treated with lime, yielded the artificial saccharoid substance methylenitan (1861).

Butlerov combined his lecture course in organic chemistry with work on the theoretical principles of the science

In 1868, upon D. Mendeleev's nomination, Butlerov was elected a professor of the University of St. Petersburg. In 1874 he became a member of the Russian Academy of Sciences.

he read at a congress of German naturalists and physicians in Speyer on September 19, 1861.

"The chemical nature of a complex particle is determined by the nature of its elementary constituent parts, their number and chemical structure." This was Butlerov's basic postulate. All the atoms of a molecule of a complex substance interacted with one another; mutual influence was strongest between directly linked atoms and less pronounced between the atoms of elements linked through other atoms. The distribution of this interaction, determined by the manner in which the atoms in a molecule were linked, was termed by Butlerov *chemical structure*.

Could chemical structure be determined? Butlerov answered this question in the affirmative: "The possibility of assessing chemical structure is adequately confirmed by the present state of our knowledge."

Isomerism of Carbon Compounds. In organic chemistry, unlike inorganic, a very big part is played by the phenomenon of isomerism.

In carbon compounds, as stated above, one and the same molecular formula corresponds not to one, but to several compounds, which differ in physical and chemical properties. This phenomenon was discovered a long time ago. In 1830 Berzelius gave it the name of "*isomerism*". Even among the relatively simple compounds of carbon there are numerous isomers. For instance, upwards of twenty different substances are known—all having the composition $C_4H_8O_2$ —which differ drastically in physical and chemical properties and sometimes even belong to different classes; some of them are acids (butyric and isobutyric acids), while others are neutral substances (e.g., dioxane). Eighty substances described in the literature correspond to the composition $C_6H_{12}O_2$, and there are countless other examples of this.

Butlerov's theory of chemical structure provided a sound explanation of isomerism.

Butlerov pointed out, in his examination of the phenomenon of isomerism, that the atoms of isomeric molecules of one and the same composition could be connected in a different manner: "Only a certain difference in this relationship (a difference in the manner of linkage) can account for the phenomena of isomerism." In other words, isomerism is due to a difference in the system of linkages in the molecule.

Principal Methods of Determining Chemical Structure. In defiance of the theory of types, Butlerov maintained that a compound

* From the Greek word *meros* (part), which, with the prefix *iso*, means "composed of the same parts".

could have only one structural formula, which should reflect all its properties.

"A conclusion concerning the chemical structure of substances can, in all probability, best be confirmed by studying the methods of their synthetic formation, primarily syntheses taking place at but slightly increased temperatures and—in general—at conditions enabling us to follow the process whereby the chemical particle gradually becomes more complicated." This principle is followed constantly in chemistry. In such conditions, as a rule, there is a breakdown of one or several linkages; radicals and residues are redistributed, but their structure remains intact.

Typical examples of this are: the preparation of hydrocarbons by the Wurtz reaction (p. 52), the reactions of ether (p. 167) and ester (p. 233) formation, syntheses with the aid of organometallic compounds (p. 118), syntheses involving malonic ester (see p. 254), etc.

"...Analytical reactions can also serve to determine chemical structure: if, for instance, a body undergoes a definite decomposition under some mild influence, it must be assumed that the simple substances or groups (radicals) originating from it existed as such in the decomposed particle."

The first stage in studying the structure of natural compounds is, as a rule, their decomposition, the systematic destruction of a complex substance. This technique is employed in investigating the structure of fats, sugars, proteins, natural rubber, vitamins, antibiotics, and many other substances.

A century has now passed since these principles were established, but the progress of organic chemistry has only confirmed and supplemented them. True, along with reactions following this basic "*principle of least change*", there are also reactions in which the structure of radicals undergoes more or less pronounced changes. But these departures usually likewise obey certain rules.

Butlerov could not in his day propose that physical methods be used extensively, since there were not sufficient data for this and physics in that period did not have at its command the means that it has today. He did, however, foresee the possibility of using the physical properties of substances to determine their structure. These problems are dealt with in a lengthy chapter in his textbook *An Introduction to a Comprehensive Study of Organic Chemistry*.

The study of the optical and electrical properties of organic substances often provides modern science with a means not only of determining the relative positions of the atoms in a molecule more rapidly and exactly, but also of obtaining quantitative characteristics of the strength of the bonds between the atoms and estimating the distances between the atoms in absolute units.

In our elementary course we can only touch upon the application of physical methods to organic chemistry. This is done in the paragraphs devoted to determining dipole moments (p. 63), molecular refraction (p. 83), and the rotation of the plane of polarization (p. 145 fol.).

The course *An Introduction to a Comprehensive Study of Organic Chemistry* was especially important in helping to spread the new theory. In his course, Butlerov marshalled systematic and extremely convincing evidence proving the correctness of the principles of his theory, applicable to all classes of organic compounds; he demonstrated how, applied to specific cases, his theory provided a key to determining the structure of a substance.

Butlerov boldly predicted the possibility of preparing a number of new organic substances and even of whole classes of compounds.

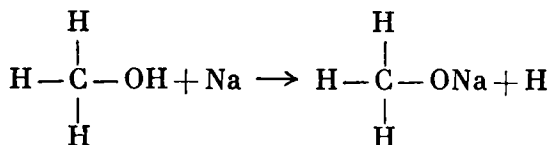
In his subsequent experimental work he was able to synthesize some of the compounds he had predicted: the second of the two possible butanes, isobutane (1867); the first representative of the tertiary alcohols, trimethylcarbinol (1864), and trimethylacetic acid (1872).

His disciples—V. Markovnikov, A. Zaitsev, Y. Wagner, A. Popov, and others—succeeded in synthesizing many other new compounds the possibility of whose existence followed from the Butlerov theory.

The Mutual Influence of Atoms in Chemical Compounds. The chemical character of this or that atom and its behaviour in reactions are determined both by the nature of the atom and by its position in the molecule.

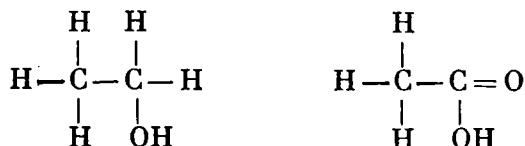
The hydrogen atoms in methyl alcohol thus differ very drastically in their reactivity.

Of the four of them, only one—the hydrogen of the hydroxyl—can be replaced by the action of metallic sodium:

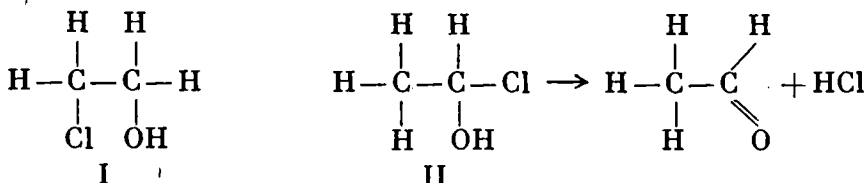


A marked influence is exerted not only by the atoms of elements directly linked to the hydrogen, but also by neighbouring atoms ("indirectly linked atoms").

Ethyl alcohol and acetic acid contain hydroxyl groups, but the hydrogen atoms in these groups differ in their behaviour. This is due to the fact that in acetic acid there is an oxygen atom next to the hydroxyl:



The closer atoms are to one another, the more pronounced their mutual influence. For instance, ethylene chlorohydrine with the structure (I) is quite stable, whereas its isomer of structure (II) is unstable and releases hydrogen chloride spontaneously:



There are numerous examples of such mutual influence of atoms inside molecules in chemistry, and we come across them all the time. The idea of the mutual influence of atoms is the cornerstone of Butlerov's theory.

This problem was dealt with in many papers by Butlerov and his disciples. Thus V. Markovnikov's D.Sc. dissertation (1869) bore the title "Data on the Problem of Atomic Interaction in Chemical Compounds". The regularities he established governing the linkage of atoms to a double bond of a hydrocarbon will be explained elsewhere in this book (p. 77).

Thus, when speaking of Butlerov's theory of chemical structure, we must clearly grasp the following points:

Initial premises:

1. Atoms, and the molecules they make up, exist in reality.
2. The structure of the molecules of a substance can be established experimentally.

Basic principles of the theory:

3. The properties of substances are determined by their qualitative and quantitative composition and by the chemical structure of their molecules.

4. Chemical structure is the order in which the atoms of a molecule are linked. For every substance there can be only one formula showing chemical structure.

5. The atoms of a molecule influence one another. Atomic interaction is strongest among atoms linked directly; it is much weaker among atoms not linked directly.

Methods of determining chemical structure:

6. Chemical structure can be determined by studying the chemical transformations of a substance. In chemical transformations under mild conditions the structure of groups does not change (principle of least change).

7. The theory of the constant valency of elements and the theory of the linkage of identical atoms (especially C—C) can help in establishing chemical structure.

New possibilities opened up by the theory:

8. A real explanation of homology and isomerism, and also the prediction of new organic substances and their properties.

9. The general scientific classification of organic compounds.

Our new insight today into the nature of chemical bonds is providing more and more additional support for the regularities discovered and the general conclusions drawn from them.

11. Classification of Organic Compounds. "A chemical classification will be natural if the principal criterion for grouping some bodies together and separating others is their similar or different chemical structure, whilst their nature is determined by the nature of their components, their amount, and the chemical structure of the particle." This was what Butlerov required for a scientific classification of organic compounds. Consequently, compounds of similar structure should be referred to the same class.

The C—C and C—H bonds, which usually undergo little change in typical reactions, are chemically least active. For this reason the chemical character of organic compounds is determined primarily by the presence of halogen, oxygen, nitrogen, and other atoms in the molecule. In this way, compounds containing the groups

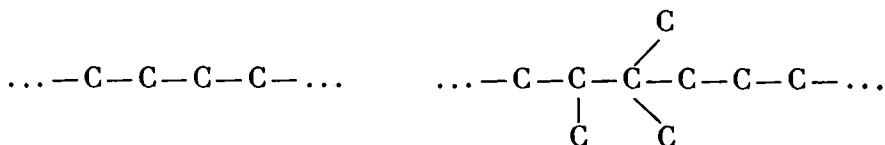
$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C} \\ \backslash \\ \text{OH} \end{array}$ and $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S} \\ \parallel \\ \text{O} \end{array} \text{OH}$ are acids, while the $-\text{NH}_2$ group imparts

a basic character to a substance.

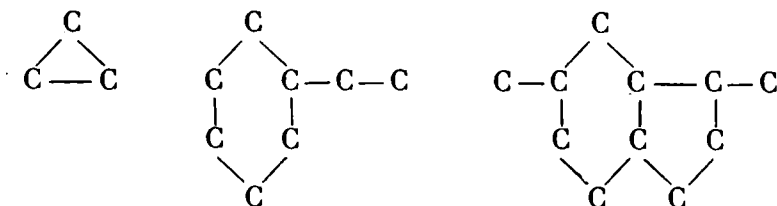
Such groups are called *functional*. The part of a complex organic substance most stable and least subject to change is thus its hydrocarbon part and, especially, the carbon chain or *carbon skeleton*.

The three main divisions of organic chemistry are determined by the structure of this, as it were, mainstay of a compound, the carbon skeleton.

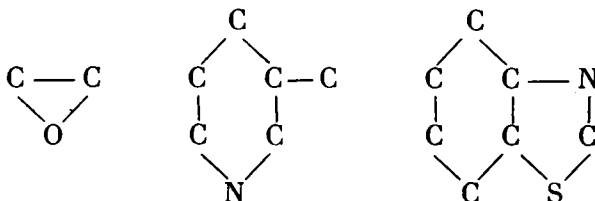
A. Acyclic (Aliphatic) Compounds. Their skeleton consists of directly linked carbon atoms in the form of an open—straight or branched—chain:



B. Carbocyclic Compounds. Their molecules have cyclic carbon chains:



C. Heterocyclic Compounds. They contain cyclic systems that include atoms of other elements besides carbon:



The compounds in each division have characteristic features.

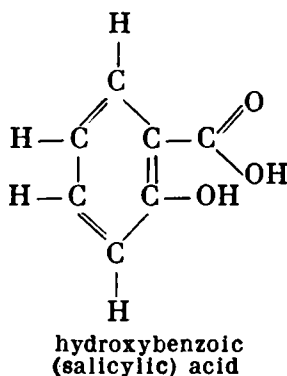
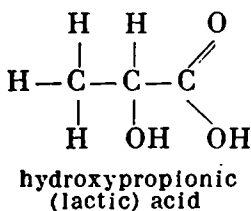
Within each division, compounds are subdivided into *classes* according to their functional groups.

The simplest compounds of all are the hydrocarbons of the saturated and the unsaturated series.

The more complicated compounds can be represented as having originated from this or that hydrocarbon through the replacement of one or several hydrogen atoms by corresponding atoms or atomic groups. This gives rise to the classes of hydroxy compounds (mono- and polyhydroxy alcohols, with one or several OH groups), oxo compounds, which contain C=O groups (aldehydes and ketones), carboxylic acids, with COOH carboxyl groups, etc.

The molecule of an organic compound can also contain several different functional groups.

The hydroxy acids are a case in point:



Each of these functional groups, while essentially retaining its chemical character, exercises an influence on other groups and is itself influenced by neighbouring atoms.

The classification of organic compounds is thus founded on the similarities and differences in their structure, reflected by structural formulas; the classification is genetic, i.e., indicating the evolution (genesis) of a given complex compound from a simple hydrocarbon.

It is this characteristic feature that is reflected in Schorlemmer's definition of organic chemistry, quoted above (p. 19), as the chemistry of hydrocarbons and their derivatives.

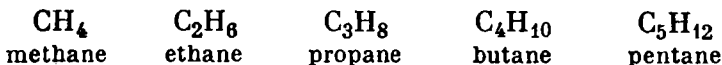
Part One
COMPOUNDS
WITH AN OPEN CHAIN
OF CARBON ATOMS

Hydrocarbons

SATURATED HYDROCARBONS

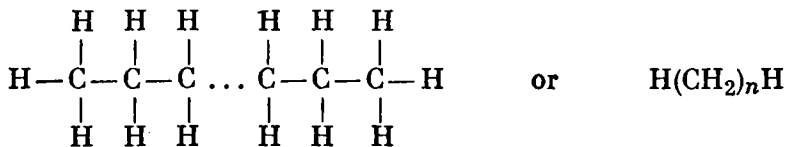
Saturated hydrocarbons, or paraffins, are hydrocarbons in whose molecules the carbon atoms are linked by single bonds, while all the valency units not used up to link the carbon atoms are saturated by hydrogen atoms.

12. Homologous Series of Saturated Hydrocarbons. The simplest saturated hydrocarbons are:



Next in the series comes C_6H_{14} (hexane), then C_7H_{16} (heptane), C_8H_{18} (octane), C_9H_{20} (nonane), and so on, followed by still more complex compounds, such as $\text{C}_{60}\text{H}_{122}$ (hexacontane) and $\text{C}_{70}\text{H}_{142}$ (heptacontane). Each consecutive member of the series differs from the preceding one by a CH_2 group.

Substances of similar structure that differ in composition by one or several CH_2 groups are called *homologues*. A group of homologues make up a *homologous series*. In this particular case it is the homologous series of saturated hydrocarbons, or paraffins. Let us assume that we have a saturated hydrocarbon with a straight chain of n carbon atoms:



Each of these carbon atoms is linked with two hydrogen atoms; besides this, each of the two extreme carbon atoms is linked with another hydrogen atom. Consequently, the total number of hydrogen atoms is $2n + 2$, and the general composition of the saturated hydrocarbons can be expressed by the formula $\text{C}_n\text{H}_{2n+2}$. It will be clear from subsequent pages that this formula also holds true for saturated hydrocarbons with branched carbon chains.

The saturated hydrocarbons are the richest of all hydrocarbons in hydrogen: each carbon atom in the hydrocarbon molecule is linked

with the maximum possible number of hydrogen atoms, and the *highest limit of carbon saturation with hydrogen* is thus reached. Hence the name *saturated*, or *limit*, hydrocarbons.

The names of the hydrocarbons of this series have the same ending "ane". The first part of the name of the hydrocarbons from C_5 onward is derived from the Greek numerals indicating the number of carbon atoms, e.g., the hydrocarbon C_5H_{12} is called pentane; C_6H_{14} , hexane; C_7H_{16} , heptane; C_8H_{18} , octane; C_9H_{20} , nonane, etc.

A quantitative change in the composition of the molecule, caused by the addition of a CH_2 group to the preceding member of the series, produces a qualitatively different substance. This is one of the most striking illustrations of the law of nature concerning the transition of quantity into quality.

This law may be traced through the whole of chemistry. F. Engels wrote: "Chemistry can be termed the science of the qualitative changes of bodies as a result of changed quantitative composition."

The main credit for investigating the homologous series of the paraffins is due to C. Schorlemmer*. In a reference to the significance of Schorlemmer's work on the hydrocarbons of the paraffin series, Engels wrote: "The knowledge that we have about the paraffins at present we owe chiefly to Schorlemmer. He investigated the then known compounds belonging to the paraffin group and isolated one type from another, obtaining many of them in pure form for the first time. Other members of the series, which in theory should have existed, but in reality had not yet been found, were discovered by him, and it was he too who prepared them. He thus became one of the founders of modern scientific organic chemistry."

13. Hydrocarbon Radicals (Alkyls). If a molecule of a saturated hydrocarbon is made to give up one hydrogen atom, the remainder is called a *monovalent radical*. These radicals cannot be isolated in the free state**, but the idea of radicals can be used in forming the names of complex hydrocarbons and other organic compounds. The names of radicals are derived from the names of the corresponding saturated hydrocarbons by substituting the ending *yl* for the ending *ane*.

* Carl Schorlemmer (1834-92). Born in Germany. In 1858 moved to England. From 1874 was Professor of Organic Chemistry at Manchester. Schorlemmer was a participant in the First International, a communist and a friend of F. Engels and K. Marx. His major work was done in the study and synthesis of the saturated hydrocarbons. His investigations refuted the claim that ethane exists in two isomeric forms; he was able to prove that both "ethane isomers" are identical and are one and the same dimethyl CH_3-CH_3 . This was of great theoretical importance and played an outstanding part in the history of organic chemistry. Schorlemmer's textbooks of chemistry (written in collaboration with Roscoe) were widely known.

** The possibility of the short-lived existence of so-called "free radicals" in chemical reactions will be discussed later (p. 481).

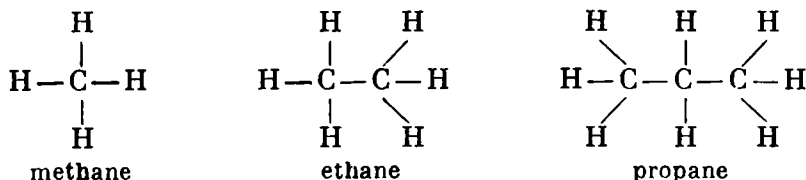
Hydrocarbon		Radical	
CH_4	methane	$-\text{CH}_3$	methyl
C_2H_6	ethane	$-\text{C}_2\text{H}_5$	ethyl
C_3H_8	propane	$-\text{C}_3\text{H}_7$	propyl
C_4H_{10}	butane	$-\text{C}_4\text{H}_9$	butyl
C_5H_{12}	pentane	$-\text{C}_5\text{H}_{11}$	amyl
C_6H_{14}	hexane	$-\text{C}_6\text{H}_{13}$	hexyl
C_7H_{16}	heptane	$-\text{C}_7\text{H}_{15}$	heptyl

The exception to the rule in the case of the C_5H_{11} radical (amyl) is due to the fact that the names of the simplest radicals appeared before the names of the hydrocarbons themselves. They were formed from the names of the alcohols (methyl, ethyl, ... amyl). It is for this reason that the hydrocarbon radicals are often grouped under the common name of *alkyls*.

The names of the radicals can serve as a basis in forming the names of many organic compounds:

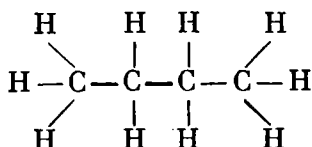
CH_3I methyl iodide
 $\text{C}_5\text{H}_{11}\text{Br}$ amyl bromide
 $\text{C}(\text{CH}_3)_4$ tetramethylmethane, etc.

14. Structure of Saturated Hydrocarbons. Every saturated hydrocarbon may be derived from the preceding member of the homologous series by substituting a methyl radical for one of the hydrogen atoms. This adds a CH_2 (methylene) group to the molecule. In this way from methane we obtain ethane; from ethane, propane:

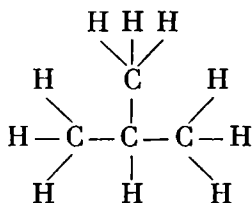


In the molecules of methane and ethane all the hydrogen atoms are absolutely equivalent in position, and it is of no consequence which of them the methyl group replaces. This is in agreement with the fact that the first three members of the paraffin homologous series have no isomers.

But in the propane molecule the hydrogen atoms are not all equivalent. The hydrogen atoms attached to the extreme carbon atoms differ in their position from the hydrogen atoms attached to the middle carbon atom. The substitution of a methyl group for a hydrogen atom in the propane molecule may therefore take two different courses: the hydrogen atom replaced may be either one attached to the middle carbon atom or one attached to an extreme carbon atom. In the latter case the substitution produces normal butane:

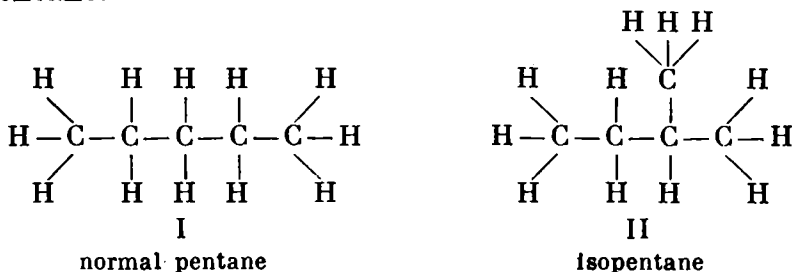


The replacement of a hydrogen atom attached to the middle carbon atom gives isobutane:

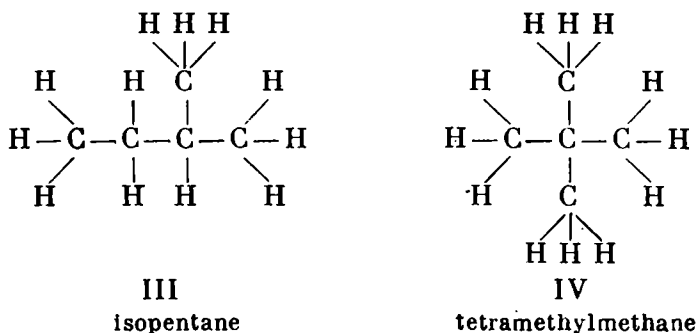


The composition of both substances is expressed by one and the same formula C_4H_{10} : normal butane and isobutane are isomers. This isomerism of butane was discovered by Butlerov, who in 1867 synthesized isobutane.

In the molecule of normal butane there are two types of hydrogen atoms: those that belong to the CH_3 groups situated symmetrically at the ends of the chain and those that belong to the CH_2 groups in the middle of the chain. Accordingly, from normal butane we can derive two hydrocarbons of the composition C_5H_{12} , normal pentane and isopentane:



In the molecule of isobutane there are likewise two types of hydrogen atoms: nine of them belong to absolutely identically situated CH_3 groups and differ in position from the tenth hydrogen atom. Consequently, from isobutane we can also derive two hydrocarbons:



Two of the above four structural formulas (II and III) are absolutely identical. Three isomers are thus possible (and are, indeed, known) for the hydrocarbon of C_5H_{12} composition: normal pentane, isopentane, and tetramethylmethane. The latter name is due to the

fact that tetramethylmethane may be looked upon as methane CH_4 in which methyl groups have been substituted for all the hydrogen atoms.

As we move from the lower to the higher members of the series, the number of theoretically possible isomers increases very rapidly:

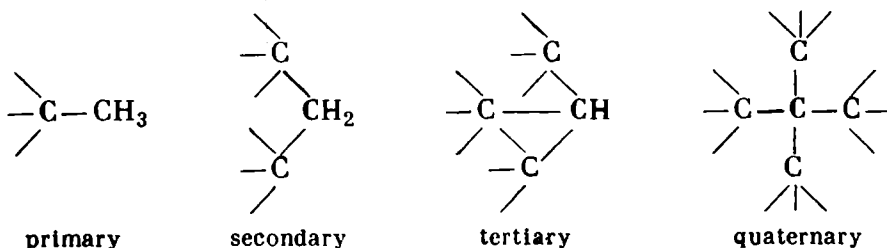
Number of carbon atoms in molecule	1	2	3	4	5	6	7	8	9	10	11	12	13
Number of isomers	1	1	1	2	3	5	9	18	35	75	159	355	803

The graphic structural formulas in this paragraph clearly illustrate the manner in which all the atoms in the molecule are linked. In another system of structural formulas frequently used in organic chemistry the bonds between the carbon atoms are denoted by dashes*.

Ethane	CH_3-CH_3
Propane	$\text{CH}_3-\text{CH}_2-\text{CH}_3$
Butane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$
Pentane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$
Isobutane	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}-\text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array}$
Isopentane	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}-\text{CH}_2-\text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array}$
Tetramethylmethane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$

Compounds with unbranched carbon chains, such as butane and pentane, are called compounds of *normal structure*; if the chain, on the other hand, is branched, the compounds are said to be of *isostructure*. Isobutane and isopentane are examples of isostructural compounds.

A carbon atom attached to only one other carbon atom is called *primary*; a carbon atom attached to two others is said to be *secondary*; to three, *tertiary*, and to four, *quaternary*:



* In the old literature, dots are sometimes used instead of dashes, e.g., $\text{CH}_3 \cdot \text{CH}_3$.

In the above examples the primary, secondary, etc., carbon atoms are in bold type.

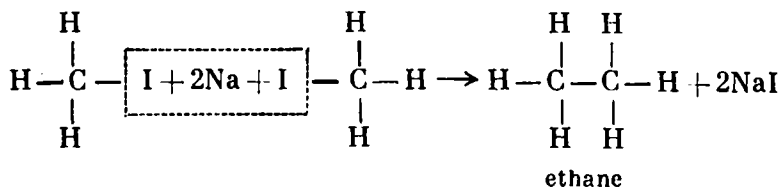
In the molecules of hydrocarbons of normal structure there are only primary and secondary carbon atoms. The molecules of isostructural compounds contain tertiary or quaternary carbon atoms. In the molecule of isobutane the tertiary carbon atom uses up three valency units for linking with three other carbon atoms and one for linking with a hydrogen atom. Each of the three other carbon atoms uses one valency unit for linking with the tertiary carbon atom and the remaining valency units for linking with three hydrogen atoms; for this reason the isobutane molecule has one tertiary and three primary carbon atoms.

15. Natural Occurrence of Saturated Hydrocarbons and Their Preparation. Saturated hydrocarbons are highly widespread in nature. Methane is the principal component of natural gas, which is used extensively for industrial and household needs. Besides methane, natural gas also contains (in smaller quantities) other of the lower homologues of the paraffin series. Methane is evolved at the bottom of marshes and in coal mines; it is also formed in the dry distillation of wood, peat, and coal.

There are vast quantities of saturated hydrocarbons in some types of petroleum. Solid saturated hydrocarbons are the main component of bitumens, asphalts, and ozocerite (mineral wax). Spectral analysis findings reveal that there are very large amounts of methane in the atmosphere of the larger planets: Jupiter, Saturn, Uranus, and Neptune.

The most important of the laboratory methods for preparing saturated hydrocarbons is the *Wurtz reaction**, discovered in 1854. It consists in the heating of alkyl halides with metallic sodium. Two examples are given below.

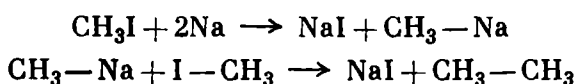
Ethane C_2H_6 can be obtained by the action of metallic sodium on methyl iodide:



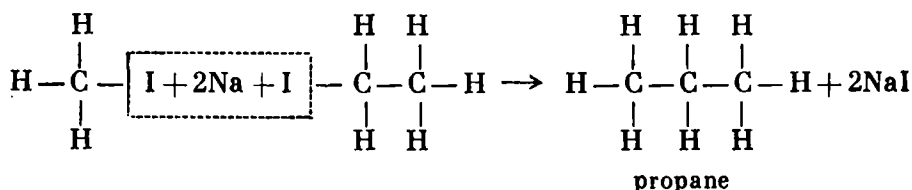
* Charles Adolphe Wurtz, French chemist (1817-84). Carried out extensive research in organic chemistry. Discovered a reaction for synthesizing saturated hydrocarbons (by the action of metallic sodium on halogen derivatives) and reactions for preparing and detecting fatty amines. In 1859 Wurtz obtained ethylene glycol ("double water type"), the first representative of the dihydroxy alcohols.

Two atoms of sodium deprive two molecules of methyl iodide of one iodine atom each. This leaves the carbon atoms each with one valency free, and they thereupon saturate each other, forming a molecule of ethane.

This general pattern of the reaction does not, however, reveal its mechanism, which is in most cases much more complicated. The investigations of P. Shorygin and other chemists have shown that in the Wurtz reaction the sodium at first replaces the halogen, after which the sodium derivative reacts with the alkyl halide:



Propane C_3H_8 can be prepared by treating a mixture of methyl iodide and ethyl iodide with metallic sodium*:

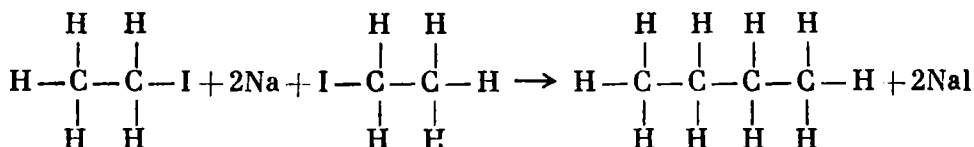


The Wurtz reaction can also be used to establish the structure of the resulting hydrocarbons. As stated above, in chemical reactions proceeding under moderate conditions the structure of radicals remains unchanged; therefore, the structure of the hydrocarbon is determined by the structure of the alkyl halide chosen for the reaction.

The establishment of the structure of butane can serve as an example of this.

As said earlier, two isomers are known for butane C_4H_{10} : normal butane and isobutane. The former is a gas, which liquefies at -0.5° ; the latter is likewise a gas, but it liquefies only at -11.7° .

The action of metallic sodium upon ethyl iodide can only produce a hydrocarbon with the structure of normal butane:



Experiments show that its boiling point is -0.5° . Consequently, the hydrocarbon which liquefies at -11.7° must have the structure of isobutane.

16. Physical Properties of Saturated Hydrocarbons. The physical properties of some saturated hydrocarbons are given in Table 1.

* The reaction, evidently, also yields ethane (from two molecules of methyl iodide) and butane (from two molecules of ethyl iodide).

TABLE 1. Physical Properties of Saturated Hydrocarbons

Hydrocarbon	Formula	Physical state at ordinary temperature	Temperature, °C		Density (in liquid state) at °C
			melting point	boiling point	
Methane	CH ₄	Gas	-182.5	-161.6	0.416 (-161.6°)
Ethane	C ₂ H ₆	"	-183.3	-88.6	0.5462 (-88.6°)
Propane	C ₃ H ₈	"	-187.6	-42.1	0.5824 (-42.1°)
<i>n</i> -Butane	C ₄ H ₁₀	"	-138.3	-0.5	0.5788 (20°)
Isobutane	C ₄ H ₁₀	"	-159.6	-11.7	0.5592 (20°)
<i>n</i> -Pentane	C ₅ H ₁₂	Liquid	-129.8	36.07	0.6264 (20°)
Isopentane	C ₅ H ₁₂	"	-159.9	27.9	0.6199 (20°)
Tetramethylmethane	C ₅ H ₁₂	Gas	-16.6	9.5	0.613 (0°)
<i>n</i> -Hexane	C ₆ H ₁₄	Liquid	-95.3	68.7	0.6594 (20°)
<i>n</i> -Heptane	C ₇ H ₁₆	"	-90.6	98.5	0.6838 (20°)
<i>n</i> -Octane	C ₈ H ₁₈	"	-56.8	125.7	0.7028 (20°)
<i>n</i> -Nonane	C ₉ H ₂₀	"	-53.6	150.8	0.7179 (20°)
<i>n</i> -Decane	C ₁₀ H ₂₂	"	-29.7	174.0	0.7298 (20°)
<i>n</i> -Pentadecane	C ₁₅ H ₃₂	"	10	270.5	0.7658 (20°)
<i>n</i> -Hexadecane	C ₁₆ H ₃₄	Solid	18	287.1	0.7749 (20°)
<i>n</i> -Eicosane	C ₂₀ H ₄₂	"	36.4	309.7	0.7777 (37.4°)
<i>n</i> -Hexacontane	C ₆₀ H ₁₂₂	"	99	250	0.7203 (190.6°)
<i>n</i> -Heptacontane	C ₇₀ H ₁₄₂	"	105.2	(at 0.00001 mm Hg)	
				300	
				(at 0.0001 mm Hg)	

It will be noticed at once that the first five hydrocarbons and one of the pentane isomers, tetramethylmethane, are gases at ordinary temperature; they are followed by liquids, while the hydrocarbons beginning with $C_{16}H_{34}$ are solids. With the increase in the number of carbon atoms in the molecule, there is a rise of the density, the melting point and the boiling point. Saturated hydrocarbons with branched chains have lower boiling points than isomeric hydrocarbons with normal chains. Melting points, on the other hand, are the higher, the more ramified the carbon chain. For instance, one of the octanes, whose formula is $(CH_3)_3C-C(CH_3)_3$, melts at 100.6° , whereas the melting point of normal octane $CH_3(CH_2)_6CH_3$ is -56.8° , i.e., 157.4 degrees lower.

With the increase in molecular weight in the series of saturated hydrocarbons, there is a rise of melting and boiling points.

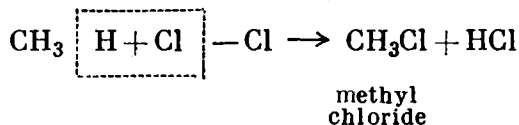
This rule, naturally, holds true only when hydrocarbons of similar structure are compared.

Methane and ethane are odourless; the liquid hydrocarbons have a specific odour, while the higher hydrocarbons are odourless.

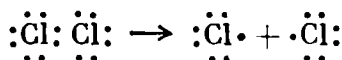
All the hydrocarbons are practically insoluble in water; their density is less than one.

17. Chemical Properties of Saturated Hydrocarbons. A distinctive feature of the saturated hydrocarbons is their chemical inertness, i.e., at ordinary temperature they do not undergo oxidation and do not react with concentrated sulphuric acid or a number of other vigorous reagents. This accounts for their name: paraffins (from the Latin *parum affinis*, which means "little affinity"). They do, however, react readily with chlorine and bromine, forming corresponding halogen derivatives. In dispersed sunlight these reactions proceed even at ordinary temperature.

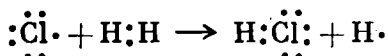
When methane is subjected to the action of *chlorine*, one atom of the latter deprives the methane of one atom of hydrogen, while the other chlorine atom takes the place of the hydrogen. The reaction results in the formation of methyl chloride and hydrogen chloride:



Reactions Involving Free Radicals. Mixed in the dark at ordinary temperature, gaseous chlorine and hydrogen react extremely slowly. To speed the reaction, the mixture has to be heated or else exposed to a bright light. It has now been established that in these conditions the neutral chlorine molecules absorb either thermal or light energy and decompose, giving rise to free atoms or radicals:

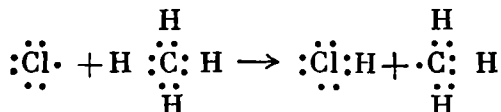


A radical contains an odd number of electrons (has an unpaired electron) and is not electrically charged, i.e., is not an ion. Reactions involving radicals are called *radical reactions*. The atoms or radicals may recombine into Cl_2 molecules with the evolution of energy or may influence the hydrogen molecule. The chlorine atom ruptures the hydrogen molecule, forming an HCl molecule and a free hydrogen atom:



The atomic hydrogen may, in turn, attack the chlorine molecule, forming a hydrogen chloride molecule and atomic chlorine. This gives rise to a *chain reaction*, which can produce an explosion.

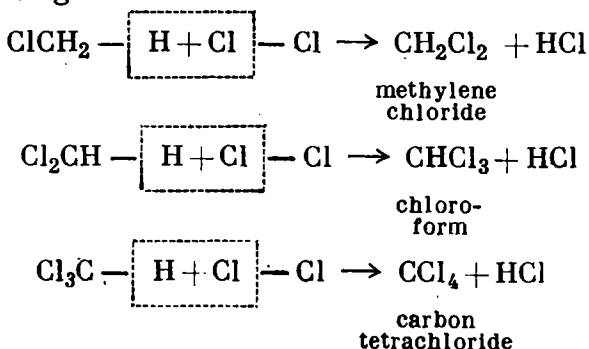
Chlorine can react similarly with saturated hydrocarbons, for example, with methane. A free chlorine atom removes a hydrogen atom from the methane molecule, producing HCl and a free methyl radical:



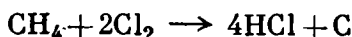
Like the reaction between chlorine and hydrogen, this reaction generates energy, with the result that an autoaccelerating reaction sets in and may cause an explosion of the gaseous mixture. The free methyl—and hydrocarbon radicals in general, for that matter—survive only for minute fractions of a second. They can either promote the chlorination reaction on encountering chlorine or else recombine. The chain of radical transformations may be cut short when radicals encounter other radicals, the walls of the vessel, or impurities.

The discovery and study of the mechanism of chain reactions by N. Semyonov and his school was of tremendous importance for an understanding of photochemical processes, oxidation reactions, polymerization, etc.

Along with the formation of methyl chloride, there is further replacement of the hydrogen by chlorine, with a mixture of various substances resulting:



Direct sunlight causes the interaction of methane and chlorine to proceed explosively, with the formation of hydrogen chloride and release of carbon:

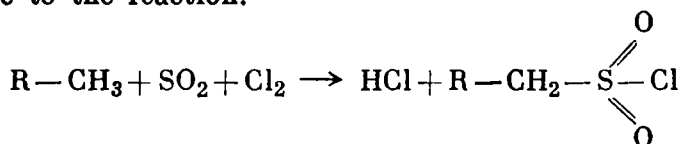


The ability of chlorine to replace hydrogen in organic compounds was discovered as far back as 1793 by T. Lovits, a member of the Russian Academy, who observed it in the preparation of the chloroacetic acids (p. 260); in the thirties of the past century this was noted by the French chemist Dumas.

Sulphuric acid at ordinary temperature does not act upon saturated hydrocarbons; when slightly heated, fuming sulphuric acid can have an effect upon hydrocarbons, producing sulphonic acids (p. 173). Sulphonation proceeds more readily in the case of saturated hydrocarbons of isostructure (containing the CH group).

At a high temperature sulphuric acid acts as an oxidizing agent, turning hydrocarbons into carbon dioxide and water.

In industry the reaction of *sulphochlorination* is often used to obtain sulphoderivatives. An equimolecular mixture of sulphur dioxide and chlorine is passed through a kerosene fraction of petroleum, which contains a large amount of hydrocarbons of normal structure. The mixture is illuminated with mercury vapour lamps, which emit a great deal of short-wavelength light (violet and ultraviolet). Irradiation causes the chlorine molecules to form chlorine atoms, which give rise to the reaction:

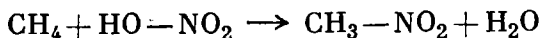


The reaction results in the formation of fatty sulphonic acid chlorides, which are used in the manufacture of detergents (p. 221).

Nitric acid at ordinary temperature has little effect upon saturated hydrocarbons; when heated, it acts as an oxidizing agent. However, as demonstrated by M. Konovalov*, weak nitric acid upon heat-

* Mikhail Konovalov (1858-1906) completed his course of studies at Moscow University in 1884. In 1896-99 was Professor at the Moscow Agricultural Institute; from 1899 on, Professor at the Kiev Polytechnical Institute. Konovalov's early papers were concerned with the nature of Caucasian petroleum. He evolved methods of isolating, purifying, and preparing various naphthene derivatives (p. 499) and studied the action of bromine and aluminium bromide on naphthenes. In 1888 Konovalov discovered the nitrating effect of dilute nitric acid when heated with saturated hydrocarbons (p. 328). His investigations in this field were summed up in his D.Sc. dissertation, "The Nitrating Effect of Nitric Acid on Hydrocarbons of Saturated Character" (1893). The method he proposed made it possible to prepare and investigate many new nitrogen compounds. He developed a method of preparing oximes (p. 183), alcohols, aldehydes and ketones from nitrogen compounds. He also made use of the reaction of nitration to determine the structure of hydrocarbons and suggested a method of separating nitrogen compounds and purifying them.

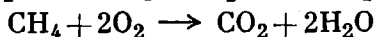
ing at increased pressure has a "nitrating" effect. The nitration of methane yields nitromethane almost exclusively:



Saturated hydrocarbons are readily nitrated in the gaseous phase at 150-175° by nitrogen dioxide or nitric acid vapours, with partial oxidation. Nowadays there are industrial installations for nitrating saturated hydrocarbons in the gaseous phase.

Oxidizing agents, even such as chromic acid mixture or potassium permanganate, have no effect at ordinary temperature on saturated hydrocarbons with normal chains. Saturated hydrocarbons whose molecules contain a tertiary carbon atom (see p. 51) are oxidized more readily.

At a high temperature saturated hydrocarbons may be ignited in the air and burn, producing CO_2 and H_2O :

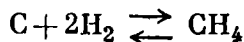


At medium temperatures these hydrocarbons (especially the solid ones) are oxidized by the oxygen of the air, this yielding oxygen-containing substances with fewer carbon atoms in the molecule; consequently, the process of oxidation is in this case accompanied by the decomposition of the hydrocarbon molecule.

To sum up. The members of the homologous series of saturated hydrocarbons are similar in structure (the molecule of each successive hydrocarbon differs from the molecule of the preceding one by a CH_2 group). Their composition may be expressed by a general formula. The members of the series have similar properties, which undergo a systematic change with the increase in the number of carbon atoms in the molecule. This shows how great an asset the concept of homologous series is in the study of organic chemistry. It is sufficient to learn the properties of the chief representative of a homologous series to have an idea of the basic properties of the other members of the series. The credit for introducing the concept of homologous series as a basic principle in classifying substances is due to Gerhardt.

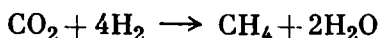
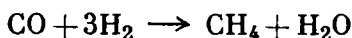
18. Methane. Methane CH_4 is often called marsh, or mine, gas. Its formation at the bottom of marshes is due to the methane fermentation of cellulose under the influence of a special type of bacteria. The decomposition of cellulose in the fore-stomach of ruminants is likewise a form of methane fermentation, owing to which the air exhaled by animals whose food contains cellulose always has methane in it. Methane is contained in the intestinal gases and the blood of animals and men. From eighty to ninety per cent of the gas contained in the cavities of coal seams and known as "fire-damp" is methane. Methane is a product of the dry distillation of wood, peat, and coal and it is also contained in natural and illuminating gas.

Methane can be obtained at a high temperature by the direct combination of the elements:

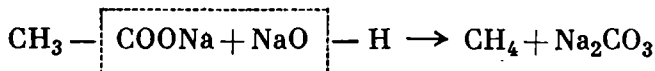


It is thus formed between the carbon electrodes of a voltaic arc in an atmosphere of hydrogen. When finely divided nickel covered with a layer of soot is heated with hydrogen, the mixture in equilibrium at 475° contains 51% methane; the nickel in this case acts as a catalyst.

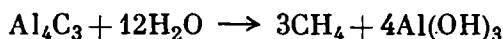
With a nickel catalyst, carbon monoxide and carbon dioxide can be reduced to methane at 250-400°:



In the laboratory methane can easily be prepared by heating sodium acetate with sodium hydroxide:



Another convenient laboratory method of preparing methane is by the action of water on aluminium carbide:

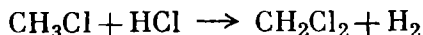
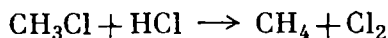


Methane is a colourless and odourless gas, with a low solubility in water; it burns with a pale flame with oxygen it forms a mixture which explodes violently upon ignition.

19. General Features of Substitution Reactions. Our examination of the above reactions of hydrocarbons prompts several general conclusions, which will later help us to gain a better understanding of the reasons for typical reaction. This applies, first and foremost to the many substitution reactions.

It will be noted at once that one of the products of such reactions is some simple and highly stable inorganic substance: HCl in chlorination, NaBr in the Wurtz reaction, Na_2CO_3 in the preparation of methane from sodium acetate, and H_2O in nitration. It is the formation of these compounds that is the prime cause of the generation of energy (heat), and, hence, determines the direction in which the reaction proceeds. For instance, the chlorination of methane is caused by the great affinity of chlorine for hydrogen, which leads to the formation of HCl, while the resulting CH_3Cl is, thermodynamically speaking, merely something in the nature of a "by-product"

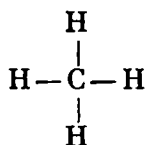
It is clear from this that such reactions as



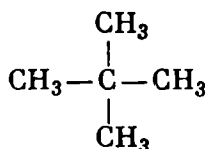
cannot proceed for thermodynamic reasons.

To avoid gross errors and get a better picture of chemical processes in organic chemistry, it is very important, especially at the beginning, to write out all the reaction products in full.

20. Geneva Nomenclature of Organic Compounds. The diversity of organic compounds makes the question of their nomenclature particularly important. An organic compound should have a name that would not only indicate the number of atoms that make up the substance, but would also give some idea of the structure of its molecule, so that its structural formula could be written easily and correctly. For example, the name "tetramethylmethane" clearly reveals that this is a substance derived from methane by the substitution of methyl groups for each of the four hydrogen atoms:



methane



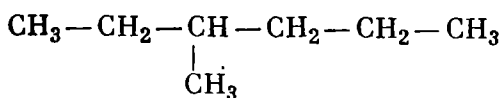
tetramethylmethane

Names like "tetramethylmethane" belong to the so-called "rational" system of nomenclature. The rules for naming compounds must be the same for all the classes of compounds.

The most convenient and universal nomenclature system is that adopted in Geneva by the International Conference of Chemical Societies in 1892. It has come to be known as the Geneva, or official, system of nomenclature.

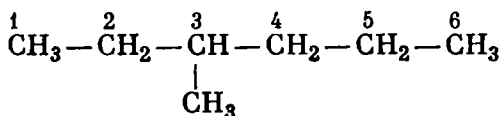
Its basic principles are the following.

The saturated hydrocarbons with normal, i.e., straight, chains are named: methane, ethane, propane, butane, pentane, hexane, heptane, octane, nonane, decane, etc. (according to the Greek numerals). The names of all the derivatives of these hydrocarbons are formed from the same roots. To form the name of some hydrocarbon with a branched chain, we must regard it as the substitution product of a normal hydrocarbon and treat the *longest carbon atom chain* in the molecule as the carbon chain of that hydrocarbon. Thus isohexane



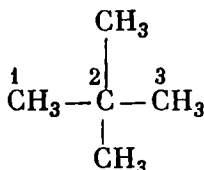
is regarded as a derivative of hexane (the longest chain), namely, as the product of the substitution of a methyl group for one of the hydrogen atoms in hexane. To form the name of this hydrocarbon, the carbon atoms of the longest chain are numbered, starting from the end nearest to the branch, and a figure is used to indicate to

which of the carbon atoms the methyl group is attached:



Isoheptane will, accordingly, under the Geneva system be called 2-methylhexane.

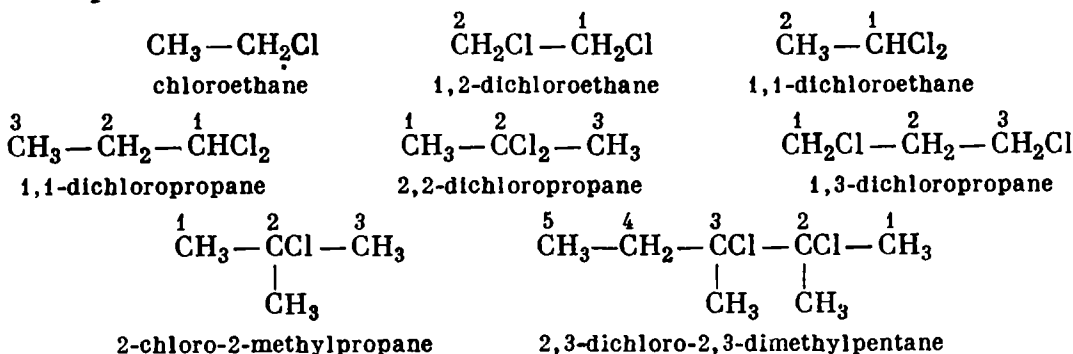
Since tetramethylmethane is the product of the substitution of two CH_3 groups for the two hydrogen atoms attached to the middle carbon atom in the propane molecule, its name in the Geneva system will be 2,2-dimethylpropane:



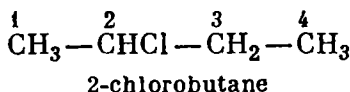
2,2-dimethylpropane

The carbon atoms which do not belong to the longest chain form side chains. In the 2,2-dimethylpropane molecule there are two side chains, each of which is a methyl group.

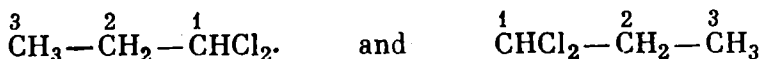
The same rules are applied in naming halogen derivatives, for example:



In the case of straight chains, the numbering is done from the end to which the halogen is closest:



Obviously, therefore, the name will not change if the formula is rewritten in the reverse order. The formulas



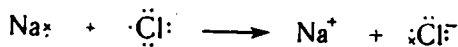
thus refer to one and the same compound: 1,1-dichloropropane.

The general name of the saturated hydrocarbons in the Geneva nomenclature is *alkanes*.

A more detailed explanation of the names of organic compounds in the Geneva nomenclature may be found on p. 580 fol.

21. Electronic Structural Schemes of Organic Compounds. According to the theory of Kossel (1916), explained in courses of inorganic chemistry, the atoms of elements, when forming chemical compounds, either give up or acquire valency electrons. As a result of this, they acquire electric charges, i.e., become ions, forming stable shells of 8 electrons.

If we designate the outer electrons of one atom by crosses and of another by dots (both crosses and dots have absolutely the same meaning and have been introduced merely for graphic illustration), we can depict the process of the combination of sodium and chlorine as follows:



The sodium atom, on giving up an electron, becomes a positive ion with an electron shell similar to that of neon; the chlorine atom, on acquiring one electron, becomes a negative ion and forms an electron shell like that of argon. The attraction between oppositely charged ions holds them together. The sodium exhibits a positive valency equal to 1, while the chlorine exhibits a negative valency likewise equal to 1.

Bonds of this type are called *heteropolar* (or electrovalent, or ionic).

Compounds whose molecules consist of ions are called *ionic*.

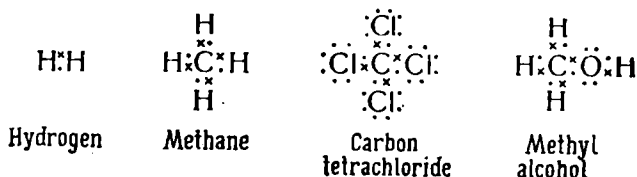
Kossel's theory, as applied to these compounds, is borne out by a large number of facts. It has been proved in various ways that the crystal lattices of these substances consist of ions and not of atoms. In aqueous solutions of compounds of the salt type, electrolytic dissociation causes the ions to separate and move independently.

At the same time there is a vast number of substances in whose molecules it has not been possible to detect ions and which are incapable of electrolytic dissociation. This applies, for example, to hydrogen H_2 , oxygen O_2 , and the overwhelming majority of organic compounds; in the latter compounds it has never been possible to discover carbon ions.

The bonds in such compounds are called *homoeopolar* or *covalent*.

The theory of covalent bonds was first put forward by Lewis in 1916. According to this theory, atoms combine into stable molecules only if a stable electron system is formed. This is achieved not through the loss or acquisition of electrons, but through a structure of the molecule in which some electrons are shared by two atoms, each bond being formed by a shared electron pair.

If we again designate the electrons of one atom by crosses and the electrons of a neighbouring atom by dots, we get the following patterns:



It is evident from these formulas that the carbon, oxygen, and chlorine atoms in these molecules are surrounded by eight electrons, or by what are called electron octets, each bond being effected by an electron pair. This being so, one atom cannot form links with more than four other atoms, since otherwise the number of electrons connecting it with the other atoms would exceed eight. The octet rule holds true for carbon, nitrogen, and oxygen. Among the compounds of other elements there are exceptions to the rule, while for many elements the rule is simply invalid.

The fact that organic compounds are non-ionic affects their reactivity and physical properties.

Reactions between substances that break up into ions are essentially reactions between the ions and are practically instantaneous. Organic substances are not ionized, and for this reason reactions involving them often take hours, rather than seconds or minutes. In many cases these reactions proceed at an appreciable speed only at increased temperatures.

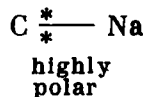
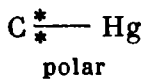
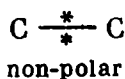
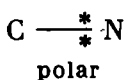
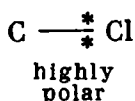
The forces of attraction between oppositely charged ions, for instance, between the sodium and chlorine ions in a sodium chloride crystal, are far greater than the forces of attraction between the molecules in crystals of organic substances. That is why, say, the melting points of most organic substances are much lower than the melting points of inorganic substances.

22. Dipole Moments. Every simple covalent bond is effected by an electron pair shared by the two atoms. This electron pair belongs to the two atoms in equal measure only if the atoms thus linked are absolutely equivalent in electric properties, as, for example, the atoms of hydrogen in a hydrogen molecule or the atoms of carbon in an ethane molecule.

When the atoms linked are not identical, the electron pair is shifted towards one of the atoms, and the bond between them is said to be polar; the atom that attracts the electron more acquires a certain surplus negative charge.

If we designate the polarity of the bond by the position of the electron pair on a line connecting the two atoms, we get the following

patterns:



Bonds in a molecule are thus distinguished by their polarity. This is one of the reasons for the different reactivity of molecules.

The term dipole moment has been introduced as a measure of the degree of polarity. When two equal and opposite charges $+e$ and $-e$ are at a distance l , the system is called a *dipole* and is characterized by a *dipole moment* μ , which is the product of the charge e and the distance l between the charges:

$$\mu = e \cdot l$$

In molecules of hydrogen H_2 and nitrogen N_2 the "electric centres" of the positive and negative charges coincide, since the common electron pairs are shared equally by the two atoms; such molecules have a dipole moment of zero and are non-polar.

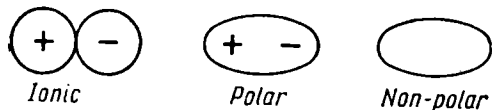


Fig. 9. Types of molecules.

In the molecules of many other substances the negative and positive charges are situated unevenly and the "electric centres" of the charges do not coincide; such molecules have dipole moments and are called polar (Fig. 9).

Since the charge of an electron equals 4.77×10^{-10} electrostatic units and the dipole length is a quantity of the same order as the diameter of the molecule, i.e., 10^{-8} cm, dipole moments are always of the order of 10^{-18} . Dipole moments are calculated, as is explained in detail in courses of physical chemistry, from the experimentally determined relationship between the dielectric constant of the substance and the temperature.

The table below gives the dipole moments of some substances:

	$\mu \cdot 10^{18}$		$\mu \cdot 10^{18}$
Hydrogen	0	Methane	0
Nitrogen	0	Ethane	0
Carbon dioxide	0	Propane	0
Carbon disulphide	0	Heptane	0
Hydrogen sulphide	1.1	Methyl chloride	1.97
Sulphur dioxide	1.61	Methylene chloride	1.59
Water	1.85	Chloroform	0.95
Ammonia	1.5	Carbon tetrachloride	0

In an electric field non-polar molecules are polarized, i.e., become dipoles. This is due to the displacement of the charges in the molecule under the influence of the electric forces of the external field. When the action of these electric forces ends, the molecules again become non-polar. Unlike *permanent dipoles*, such dipoles are called *induced*.

Molecules with permanent dipole moments can also be polarized. An external electric field has the effect of orientation on such dipoles: they tend to turn in the direction of the lines of force of the field (Fig. 10).

At the same time there takes place a certain additional polarization of the molecules: an induced dipole moment is superimposed on the permanent one.

A knowledge of the dipole moment gives us an idea of the distribution of charges in a molecule and, hence, of the symmetry of its structure. In some cases this provides a clue to the position of the atoms in the molecule.

Here are a few examples.

1. The molecules of carbon dioxide CO_2 and carbon disulphide CS_2 are non-polar. Consequently, these molecules must exhibit linear symmetry in their structure (Fig. 11).

2. The molecule of water is characterized by a considerable dipole moment. Such a molecule cannot have a structure of linear symmetry. In the water molecule the hydrogen atoms are linked with the oxy-

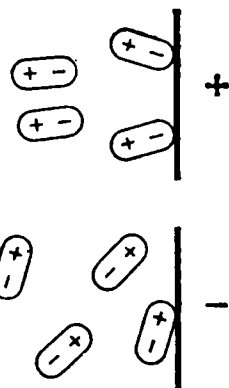


Fig. 10. Effect of external field on polar molecules.

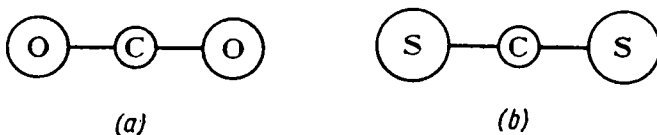


Fig. 11. Structure of carbon dioxide (a) and carbon disulphide (b) molecules.

gen atom in such a way that their bonds form a certain angle, close to 110° (Fig. 12).

3. The molecule of carbon tetrachloride CCl_4 is non-polar, although the $\text{C}-\text{Cl}$ bond is highly polar. The CCl_4 molecule is therefore symmetric, although the absence of a dipole moment in this case furnishes us with no clue as to whether the molecule is arranged in a plane or tetrahedron.

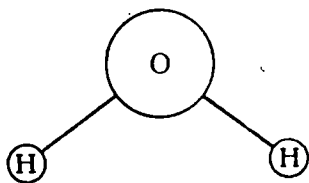


Fig. 12. Structure of water molecule.

In our subsequent description of various compounds we shall refer repeatedly to their dipole moments to account for their properties and ascertain the position of the atoms in the molecules.

It is also of practical importance to the chemist that polar substances are, as a rule, soluble in polar solvents and insoluble in non-polar solvents, while non-polar substances are soluble in non-polar solvents.

Petroleum and Natural Gas

In nature mixtures of hydrocarbons occur in the Earth's crust in the form of *petroleum*, *natural gas*, *asphalt*, and *ozocerite*.

23. Composition and Natural Occurrence of Petroleum. Petroleum is a dark brown oily liquid. As far as chemical composition is concerned, it is primarily a mixture of hydrocarbons, and is therefore their main natural source. Petroleum from different deposits differs in composition, but it invariably contains saturated, alicyclic, and aromatic hydrocarbons in varying proportions.

Apart from hydrocarbons, petroleum contains compounds of oxygen, sulphur, and nitrogen, sometimes in considerable quantities.

24. Origin of Petroleum. Several theories have been suggested to account for the origin of petroleum. According to some of them, petroleum is a product of inorganic substances; others attribute to petroleum an organic origin, from the remains of animal and plant life. The former group includes the theory of the cosmic origin of petroleum and Mendeleyev's theory.

According to the theory of the cosmic origin of petroleum, its constituent hydrocarbons were formed directly from carbon and hydrogen at an early stage in the existence of our planet. This theory accounts for the presence of considerable amounts of methane in the atmospheres of the larger planets. In Mendeleyev's opinion, petroleum was formed by the action of water on the carbides of metals (specifically, iron carbide), which make up the core of the Earth. Indeed, when carbides react with water or with dilute acids, hydrocarbons are formed, primarily methane and acetylene. Iron carbide and manganese cast iron upon interacting with water produce a petroleum-like mixture of liquid hydrocarbons. Although these facts would seem to support Mendeleyev's theory, it has now been almost completely abandoned. The nitrogen compounds contained in petroleum and its optical activity (p. 145) militate against it, serving as definite corroboration of its organic origin.

The theories of organic origin have the most supporters. Some investigators maintain that petroleum was formed from the remains of marine animals; others consider it to have been formed from the remains of marine algae, while still others trace the origin of petroleum to the remains of vegetation on land. Engler prepared a petroleum-like mixture of liquid hydrocarbons by distilling cod-liver oil under increased pressure. N. Zelinsky obtained similar products by decomposing various substances of animal and plant origin—high molecular alcohols (sterols), fatty acids, etc.—in the presence of aluminium chloride. In 1934 Treibs proved the mixed vegetable and animal origin of petroleum: all 29 petroleum samples that he investigat-

ed were found to contain derivatives of chlorophyll and haemin (95% less haemin derivatives than chlorophyll derivatives). It may therefore be assumed that petroleum was formed partly from animal and partly from vegetable matter. It is highly probable that petroleum originated from marine plankton* and marine algae, which are to be found in the seas and oceans in vast quantities.

25. Petroleum Products and Their Uses. Petroleum is the main source of petrol for internal combustion engines, as well as of lubricating oils. In addition to this, it is being used on an ever increasing scale as a raw material in the chemical industry for the synthetic manufacture of solvents, alcohols, acids, detergents, and many other valuable products. The most widespread method of petroleum refining is by distillation. The distillation products are then subjected to chemical purification in order to remove sulphur compounds and gum-forming substances.

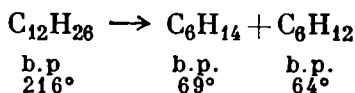
The first cut obtained in petroleum distillation is called *gasolene*. By further distillation it is made to yield *petrol* of several grades: aviation petrol, first-grade petrol, second-grade petrol, etc. The lightest fraction of this cut is *benzine*. The next cut, which boils at a temperature of 150 to 300°, serves for preparing various grades of *paraffin oil*, or *kerosene*. The residue after the paraffin oil has been distilled off is known as *fuel oil*; it is used for furnace firing. The distillation of fuel oil yields *diesel oil* (one of its uses is to make *vaseline oil*) and various *lubricants*: spindle oil, cylinder stock oil, and machine oil. The residue after the lubricants have been distilled off is called *oil tar*, which is used as a road binder. When oil tar is heated with superheated steam—or when air is passed through it during heating—it gives up its volatile admixtures and becomes synthetic asphalt. The last cut in petroleum distillation yields *petroleum jelly*, or *vaseline*, which is a mixture of solid and liquid hydrocarbons. From some grades of petroleum it is possible to isolate a mixture of solid saturated hydrocarbons called *paraffin wax*. In the U.S.S.R. the petroleum of Grozny and the Western Ukraine is rich in paraffin wax.

The progress of motor transport and aviation has created a big demand for the low-boiling fractions of petroleum, the gasolenes. Direct distillation, however, seldom yields more than 20% of gasolene. This prompted the use of casing-head gases for gasolene production.

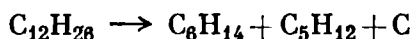
To make gasolene, casing-head gas is compressed to a small volume and passed through the coils of a cooler, which uses coolants or running water. Much of the gas is in this way condensed into gaso-

* Plankton is a term used to denote tiny marine organisms and algae, occurring usually at depths of 50 to 100 m.

lene. To extract the remaining gasolene, the gas is run through a coke-filled tower washed with diesel oil. The oil absorbs all the gasolene, which is then separated by distillation. This *gas spirit* has a low density and a low boiling point. Gasolene extraction from gas increases gasolene production, but does not raise its yield from petroleum. This can, however, be achieved by the chemical processing of petroleum and, primarily, by subjecting petroleum or its individual cuts to the *cracking process*. This is a process in which the heavy molecules of the high-boiling hydrocarbons are "cracked" into the light molecules of the low-boiling hydrocarbons that make up gasolene. For example, the hydrocarbon dodecane $C_{12}H_{26}$ can be broken down into hexane C_6H_{14} and hexene C_6H_{12} :



A dissociation process of another type proceeds simultaneously, resulting in the formation of petroleum coke:



Besides this, cracking also yields considerable amounts of ethylene and other low-molecular olefines (propylene, butylenes, and amylenes). The first industrial cracking installation was built by V. Shukhov in Russia in 1891.

In industry it is customary to distinguish *thermal* and *catalytic cracking*. In the thermal process the cracking of the hydrocarbon molecules is achieved by high temperatures (450° and higher) and increased pressure. The process is conducted in different conditions according to the initial material and the products required. *Gas-phase cracking* a process taking place in the gas phase, is conducted at a low pressure (3-5 atm) and a temperature of $550-600^\circ$. *Liquid-phase cracking* is conducted at a higher pressure (20-70 atm) and a lower temperature ($450-500^\circ$). In this case part of the initial and resulting hydrocarbons are in the liquid phase.

In the catalytic process the cracking of the hydrocarbons takes place over catalysts at lower temperatures ($450-500^\circ$) than in gas-phase cracking and at a pressure close to atmospheric. The process is conducted in the gas phase only, with various aluminium silicates in most cases serving as catalysts.

Catalytic cracking installations are more complicated and expensive, but the petrol yield is higher and the petrol is of a higher grade.

Another very widespread process of petroleum processing is *catalytic reforming*, which produces complex structural changes in the hydrocarbon molecules, but in most cases without altering the number of carbon atoms in the molecule.

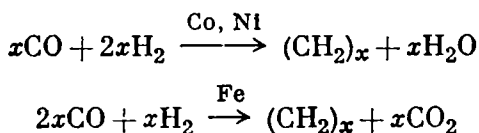
Such techniques of petroleum processing make it possible to raise the petrol yield to 80%. The bulk of the petrols is now produced in this way.

The consecutive chemical processing of petroleum hydrocarbons produces a whole series of various chemical compounds: unsaturated hydrocarbons, alcohols, acids, aldehydes, ethers and esters. All these are products of tremendous importance both for the manufacture of household goods and for technological progress. For example, the ethylene contained in cracking gases reacts with chlorine to produce dichloroethane, which is the initial material for the manufacture of polyvinyl chloride. The catalytic hydration of ethylene produces synthetic ethyl alcohol, which is an important initial material for several chemical processes. This reaction, discovered by A. Butlerov and V. Goryainov, has retained industrial importance to this day.

26. Synthetic Liquid Fuel. The fact that liquid fuel offers great advantages, as well as the fact that petroleum resources are limited, while in some countries they are lacking altogether, suggested the idea of converting coal into liquid fuel, i.e., the idea of the "liquefaction of coal".

Y. Orlov in 1908 demonstrated that when carbon monoxide and hydrogen are passed over catalysts (Ni, Pd), ethylene and other unsaturated hydrocarbons are formed. On the basis of the Orlov reaction, F. Fischer and Tropsch in 1926 developed a commercial method of liquid fuel synthesis. They proved that the passage of a mixture of carbon monoxide and hydrogen over certain catalysts at 200-300° yields saturated hydrocarbons. The catalytic agents used are metals of the eighth group (including cobalt, nickel, and iron), with the addition of other substances.

The formation of liquid and solid hydrocarbons of diverse molecular weight from carbon monoxide and hydrogen can be expressed by these equations:



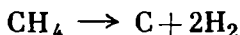
The greater part of the unsaturated hydrocarbons formed (p. 71 fol.) add hydrogen through the agency of the same catalysts to become saturated hydrocarbons.

The synthetic petrol produced by this method, known as *synthine*, is a mixture of saturated and unsaturated hydrocarbons, for the most part with normal chains.

27. Natural Gases. Asphalts. The main component of natural gases (90-98%) is methane, with ethane, propane, and the butanes

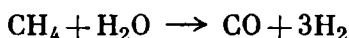
being present in smaller quantities. At times helium is present as an admixture (in some cases its content reaches several per cent).

Natural gas is an exceedingly valuable fuel. It burns up completely, leaving no ash and forming no carbon monoxide. Its calorific power is very high (about 11,000-12,000 Cal/kg), i.e., much higher than of other fuels (wood 4,700-5,100; coal 6,000-8,000; paraffin oil 10,000 Cal/kg). Not only can gas be used directly at the deposit, but it can also be carried over long distances by gas pipelines. By heating methane to 1,400-1,500°, we can obtain hydrogen and carbon (as carbon black):



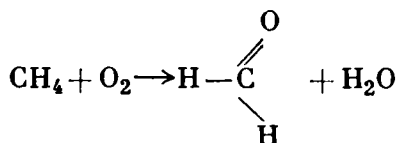
Large quantities of the carbon black obtained in this way are used by the dye industry and as an additive in the production of rubber.

The reaction of methane and steam at 700-800° over a catalyst (nickel on magnesite) produces *synthesis gas*:



which is the initial material for the production of methyl alcohol (p. 138).

The catalytic partial oxidation of natural gas in the presence of nitrogen oxides yields formaldehyde:



From formaldehyde it is possible to prepare methyl alcohol CH_3OH (p. 138), plastics (p. 382), and other products.

Asphalts consist of hydrocarbons whose molecules usually number sixteen and more carbon atoms. The best known deposits of asphalt in the U.S.S.R are on the island of Sakhalin. Sometimes asphalt permeates porous rocks. For example, near the town of Syzran and in the Caucasus there is asphaltic limestone.

Asphalt is used as an insulator, as well as in the manufacture of lacquers and roofing felt; large quantities of asphalt go into road construction.

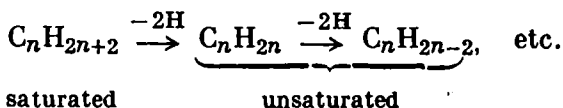
Ozocerite (mineral wax) consists for the most part of solid saturated hydrocarbons with branched chains.

By purifying ozocerite, we obtain *cerasine*, which is used as a substitute for wax in making floor polish and is also used in making oil paper and insulating materials.

UNSATURATED HYDROCARBONS

Hydrocarbons whose molecule contain fewer hydrogen atoms than do the molecules of saturated hydrocarbons with the same number of carbon atoms are called *unsaturated*.

The general formulas of the hydrocarbons are written as follows:



The series of hydrocarbons whose members differ from one another by $(2\text{H})_n$ is called *isologous*, e.g.:

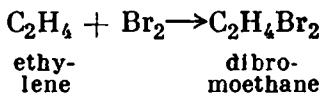


In such a series the degree of unsaturation increases.

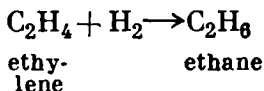
Hydrocarbons with One Double Bond (Olefines)

28. Double Bonds. Hydrocarbons with two hydrogen atoms less in their molecules than corresponding paraffins have one double bond. The general formula of such hydrocarbons is C_nH_{2n} . The simplest member of the series is ethylene* C_2H_4 .

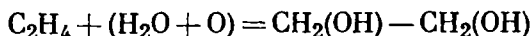
The most characteristic property of ethylene is its pronounced ability to enter into addition reactions; for instance, the ethylene molecule can add two atoms of a halogen:



or (in the presence of catalysts) two hydrogen atoms:



Another characteristic property of ethylene is its readiness to undergo oxidation. The careful oxidation of ethylene (e.g., with potassium permanganate, after Wagner**) produces ethylene glycol:



In the ethane molecule $\text{CH}_3 - \text{CH}_3$ three valency units of each carbon atom are saturated by the valency units of three hydrogen

* Methylene CH_2 does not exist in the free state. Reactions which should produce methylene invariably yield a hydrocarbon of doubled composition ethylene C_2H_4 .

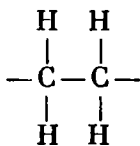
** Yegor Wagner was of the Kazan school of chemists. A pupil of A. M. Zaitsev's, he worked at St. Petersburg and Warsaw. He is known for his work in unsaturated compounds and terpenes.

atoms, while the fourth valency of each carbon is saturated by the fourth valency of the other. Since there are two hydrogen atoms less in an ethylene molecule than in an ethane molecule, the carbon atoms in the ethylene molecule must have two free valencies. This leaves room for two possibilities:

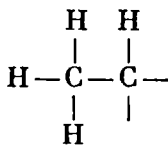
(1) the carbon atoms have a free valency each (formula I);

(2) one of the carbon atoms has both of the free valencies (formula II).

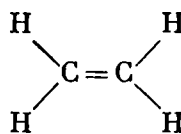
Finally, it may be assumed that the free valencies of the carbon atoms in ethylene saturate each other, i.e., that the carbon atoms in the ethylene molecule are linked by a double bond (formula III).



I



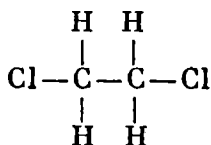
II



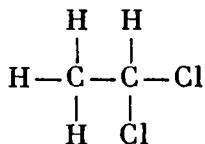
III

Which of these formulas actually does reflect the structure of ethylene?

It is perfectly clear that the addition of other substances, such as chlorine or bromine, to the ethylene molecule must take place at the expense either of the free valencies or of the valencies made available by the rupture of the second bond. If the structure of ethylene corresponds to formula I or formula III, the substance produced by the combination of ethylene and chlorine, $\text{C}_2\text{H}_4\text{Cl}_2$, must have the structure:



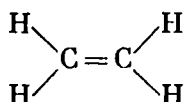
But if the structure of ethylene corresponds to formula II, ethylene must, on combining with chlorine, yield a substance of different structure:



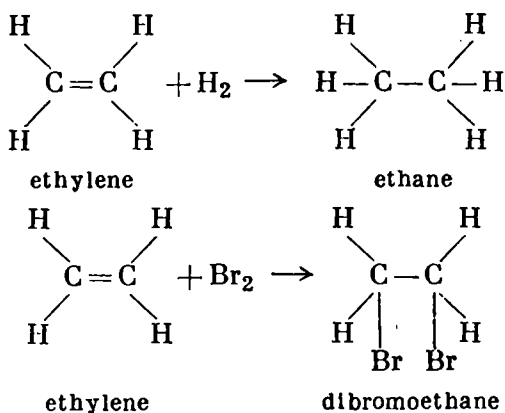
The substance resulting from the combination of ethylene and chlorine differs from the substance which is formed by the action of phosphorus pentachloride on acetaldehyde $\text{CH}_3-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array}$ and whose structure can be expressed only by the formula $\text{CH}_3-\text{CHCl}_2$. Consequently, we are led to the conclusion that the dichloroethane

molecule has the structure $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, and for this reason the structure of ethylene does not correspond to formula II.

Furthermore, the ethylene molecule always adds two atoms of a halogen or of hydrogen. It has never been possible to observe such a combination with only one halogen atom. Formula I does not account for this, and it remains quite unclear why the free valencies of the carbon atoms have to be saturated simultaneously. It therefore has to be assumed that the free valencies of the carbon atoms in the ethylene molecule saturate each other, i.e., that the carbon atoms in the ethylene molecule are linked by a double bond:



When ethylene is subjected to the action of hydrogen (by passing a mixture of ethylene and hydrogen over heated nickel) or of halogens, hydrogen or halogen atoms are added at the site of the double bond:



The symmetric structure of ethylene was established in 1868 by the investigations of A. Butlerov and M. Osokin.

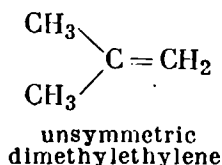
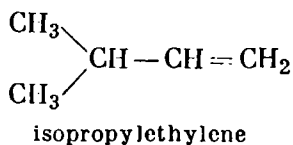
29. Olefine Nomenclature. Just as methane gives rise to a homologous series of saturated hydrocarbons, or paraffins, ethylene gives rise to a homologous series of *ethylene hydrocarbons*, or *olefines**. Every member of the series differs from the preceding or subsequent one by a CH_2 group. All the hydrogen atoms in an ethylene molecule are equivalent. Therefore, whichever hydrogen atom we replace, we can only obtain the hydrocarbon methylethylene $\text{CH}_2 = \text{CH}-\text{CH}_3$. In methylethylene there are three types of hydrogen atoms; therefore, by substituting a CH_3 group for a hydrogen atom,

* First prepared in Holland in the 18th century, ethylene chloride, which is an oily liquid, was named "oil of the Dutch chemists". For this reason ethylene is sometimes called "olefiant (oil-forming) gas".

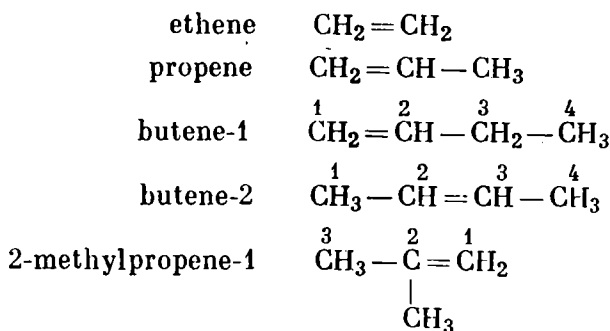
we can prepare three different olefines: ethylethylene $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$, symmetric dimethylethylene $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$, and unsymmetric dimethylethylene $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{CH}_2 \\ \diagdown \\ \text{CH}_3 \end{array}$.

These three hydrocarbons are isomeric. The isomerism of ethylethylene and symmetric dimethylethylene is due to the different position of the double bond between the carbon atoms in a normal chain. The third isomer, unlike the other two, has a branched chain. An even greater number of isomers is possible for amylene (pentene) C_5H_{10} or hexene C_6H_{12} .

The names of the ethylene hydrocarbons used to be derived from the names of alcohols with the same number of carbon atoms in the molecule: ethylene from ethyl alcohol, amylene from amyl alcohol. The isomers are often denoted by names reflecting the origin of ethylene hydrocarbons from ethylene by the substitution of alkyls for hydrogen, 'e.g.:

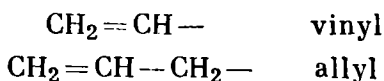


In the Geneva nomenclature the ethylene hydrocarbons have the ending *ene*: a figure after the name denotes the first carbon atom with a double bond. The numbering is done so that the double bond should be closer to the beginning:



The general name of ethylene hydrocarbons is *alkenes*.

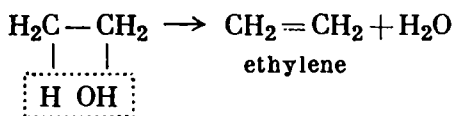
Some hydrocarbon radicals of the olefines have traditional names derived from the names of alcohols:



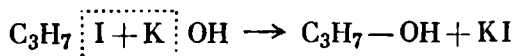
30. Preparation of Olefines and Their Structure. 1. Olefines are formed by the dry distillation of many organic substances. For this reason they are contained in coke oven gas and in oil cracking gases.

The gases formed in liquid-phase cracking contain 15% of unsaturated hydrocarbons; the gas yield is about 8% in relation to the weight of the raw material.

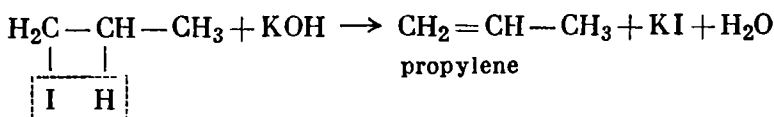
2. Olefines are prepared from alcohols by the removal of water by dehydrating agents or by the decomposition of the vapour of the corresponding alcohol at a high temperature in the presence of catalysts (Al_2O_3 , etc.):



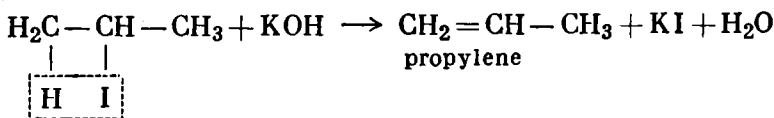
3. A very important method of preparing olefines consists in the action of a concentrated ethyl or methyl alcoholic solution of potassium hydroxide on the halogen derivatives of saturated hydrocarbons. Whereas an aqueous solution of the alkali causes the halogen to be replaced by the hydroxyl, with the formation of an alcohol,



an alcoholic solution of the alkali removes a hydrogen halide molecule forming an olefine:



propyl iodide



isopropyl iodide

Here the iodine combines with the potassium, while a hydrogen atom attached to a neighbouring carbon atom combines with the hydroxyl of the alkali. In this case we observe the operation of a general rule: hydrogen and halogen atoms are removed from neighbouring carbon atoms.

31. Physical and Chemical Properties of Olefines. Ethylene, propylene, and butylene are gases; they are followed by liquid members of the series; beginning with $\text{C}_{18}\text{H}_{36}$ the members of the series are solids (Table 2). The olefines have higher densities than do the corresponding paraffins. As in the case of the paraffins, the density and the melting and boiling points of the olefines increase with the number of carbon atoms in the molecule. Olefines with the double bond at the end of the chain have lower boiling points. For instance, 3-methylbutene-1 boils at 20.1° , while 2-methylbutene-2 boils at

TABLE 2. Physical Properties of Olefines

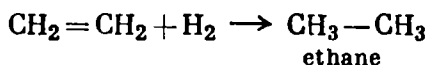
Olefine	Formula	Physical state at ordinary temperature	Melting point, °C	Boiling point, °C	Density (in liquid state) in g/cu cm
Ethylene, or ethene . .	$\text{CH}_2 = \text{CH}_2$	Gas	-169.2	-103.7	0.570 (at boiling point)
Propylene, or propene . .	$\text{CH}_3 - \text{CH} = \text{CH}_2$	Gas	-185.2	-47.7	1.5139 (at boiling point)
Ethylethylene, or butene-1	$\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$	Gas	-185.3	-6.3	0.5951 (at boiling point)
Isobutylene, or 2-methylpropene-1	$(\text{CH}_3)_2\text{C} = \text{CH}_2$	Gas	-140.3	-6.9	0.5942 (at boiling point)
Propylethylene, or pentene-1	$\text{CH}_3\text{CH}_2 - \text{CH}_2\text{CH} = \text{CH}_2$	Liquid	-165.2	30.0	0.6405
Unsymmetric methylethylene, or 2-methylbutene-1	$\text{C}_2\text{H}_5 - \text{C} = \text{CH}_2$ CH_3	Liquid	-137.5	31.2	0.6504
n-Octadecylene, or octadecene-1	$\text{CH}_3(\text{CH}_2)_{15}\text{CH} = \text{CH}_2$	Solid	17.6	314.8	0.7888

38.6; 2,4,4-trimethylpentene-1 boils at 101.4°, while 2,4,4-trimethylpentene-2 boils at 104.9.

In the olefine series, as in the paraffin series, the melting and boiling points rise with molecular weight. Like all other hydrocarbons, the olefines have a low solubility in water. Olefine vapours have a characteristic pungent odour.

The ethylene hydrocarbons have an exceedingly high reactivity. The vast majority of their reactions involve the carbon atoms linked by a double bond. The most characteristic property of the olefines is their pronounced ability to combine with other substances. One of the bonds between the doubly bound carbon atoms is in this case ruptured, and the other atoms or groups are joined to the carbon atoms by the valencies thus made available.

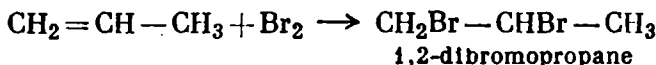
1. At a temperature of 150-200°, in the presence of finely divided nickel, olefines combine with hydrogen (*Sabatier reaction*); in this case two hydrogen atoms are added to an olefine molecule:



In the presence of powdered platinum or palladium the reaction proceeds at ordinary temperature. The reaction of the addition of hydrogen to unsaturated compounds is called *hydrogenation*.

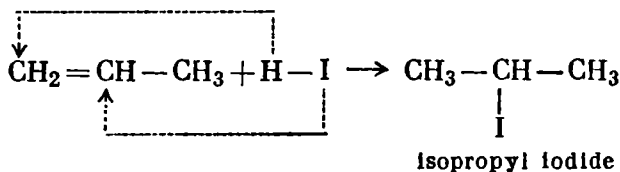
2. Olefines quite readily add halogens, especially chlorine and bromine.

Two halogen atoms are added in place of the double bond:



The reaction is used for the qualitative detection and quantitative estimation of double bonds.

3. Olefines very readily add hydrogen halides (one hydrogen halide molecule to one olefine molecule):

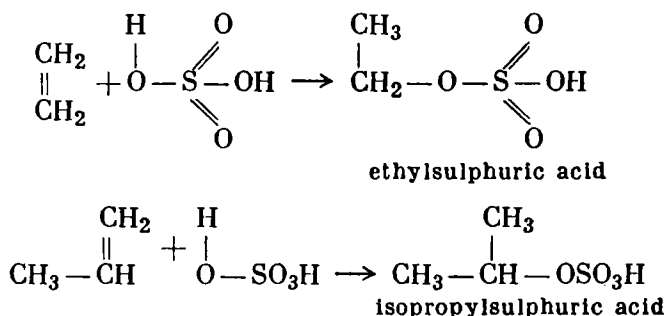


The hydrogen atom in this case becomes attached to the most hydrogenated carbon atom, i.e., the one having the greater number of hydrogen atoms. This was discovered by V. Markovnikov* (*Markovnikov's rule*).

* Vladimir Markovnikov (1838-1904) was born near Nizhny Novgorod (now Gorky). He was educated at the University of Kazan (1856-60) and afterwards worked at Butlerov's laboratory. Markovnikov synthesized several new compounds predicted by the structural theory and elaborated greatly on the ideas concerning the mutual influence of atoms in molecules; specifically, he did work

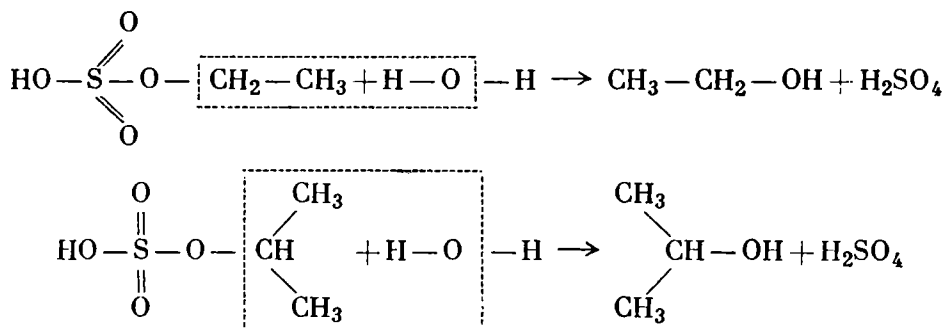
Markovnikov's rule is not absolute. In some cases, such as in the presence of peroxide substances, the addition of hydrogen bromide proceeds contrary to this rule. For instance, vinyl bromide $\text{CH}_2=\text{CHBr}$ in the absence of peroxides adds hydrogen bromide to form only 1,1-dibromoethane $\text{CH}_3-\text{CHBr}_2$, which accords with Markovnikov's rule; but in the presence of peroxides it yields primarily 1,2-dibromoethane $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$.

4. With concentrated sulphuric acid the olefines form acid esters of sulphuric acid:



In this case too the hydrogen is added to the most hydrogenated carbon atom.

The alkylsulphuric acids may be regarded as derivatives of sulphuric acid in whose molecules one hydrogen atom has been replaced by an alkyl. When alkylsulphuric acids are treated with water, alcohols are formed:

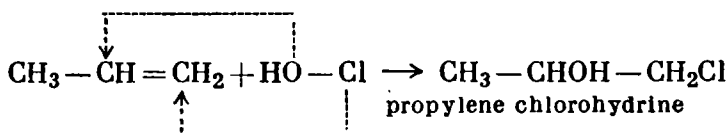


This reaction is used for the industrial manufacture of alcohols from the olefines contained in coke oven gases and oil cracking gases. It is interesting to note in this connection that as far back as 1873 Butlerov and Goryainov demonstrated that at a temperature of about 160° sulphuric acid absorbs ethylene

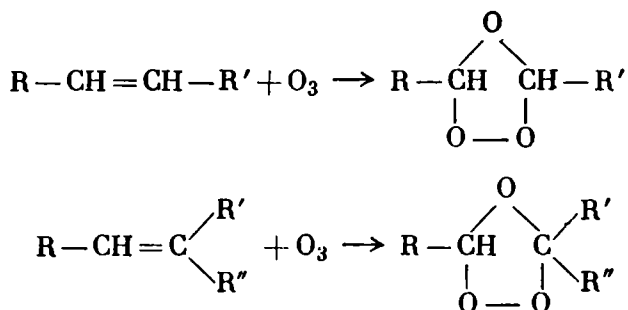
on the synthesis of isobutyric acid, oxybutyric acid, and chlorobutyric acid and studied the reactions of the addition of hydrogen halides to the double bond. He published highly interesting papers entitled "Concerning the History of the Theory of Chemical Structure", "On the Isomerism of Organic Compounds" (M.Sc. dissertation, 1865), and "Data on Atomic Interaction in Chemical Compounds" (D.Sc. dissertation, 1869). Profound thoughts on the dynamics of chemical reactions are expressed in his paper "The Principle of Chemical Equilibrium" (1902). In 1880 Markovnikov turned his attention to the composition of Caucasian petroleum. He was the first to show that petroleum contains large amounts of cycloparaffins, which he named "naphthenes".

readily. They considered that "this fact holds out promise of acquiring practical importance in the future; if an inexpensive method of preparing ethylene were found, ethylene could serve as a material for producing alcohol". Oil cracking gases have at present acquired extensive application as chemical materials for manufacturing many valuable products (p. 68).

5. Olefines add hypochloric acid; in this case the hydroxyl becomes attached to one carbon atom (the less hydrogenated), while the chlorine becomes attached to the other:

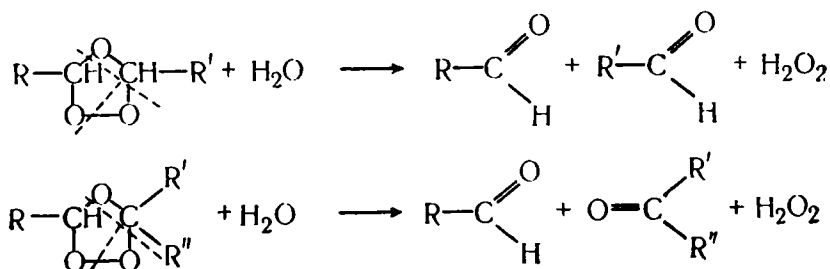


6. The action of ozone on a carbon tetrachloride solution of olefines produces ozonides:

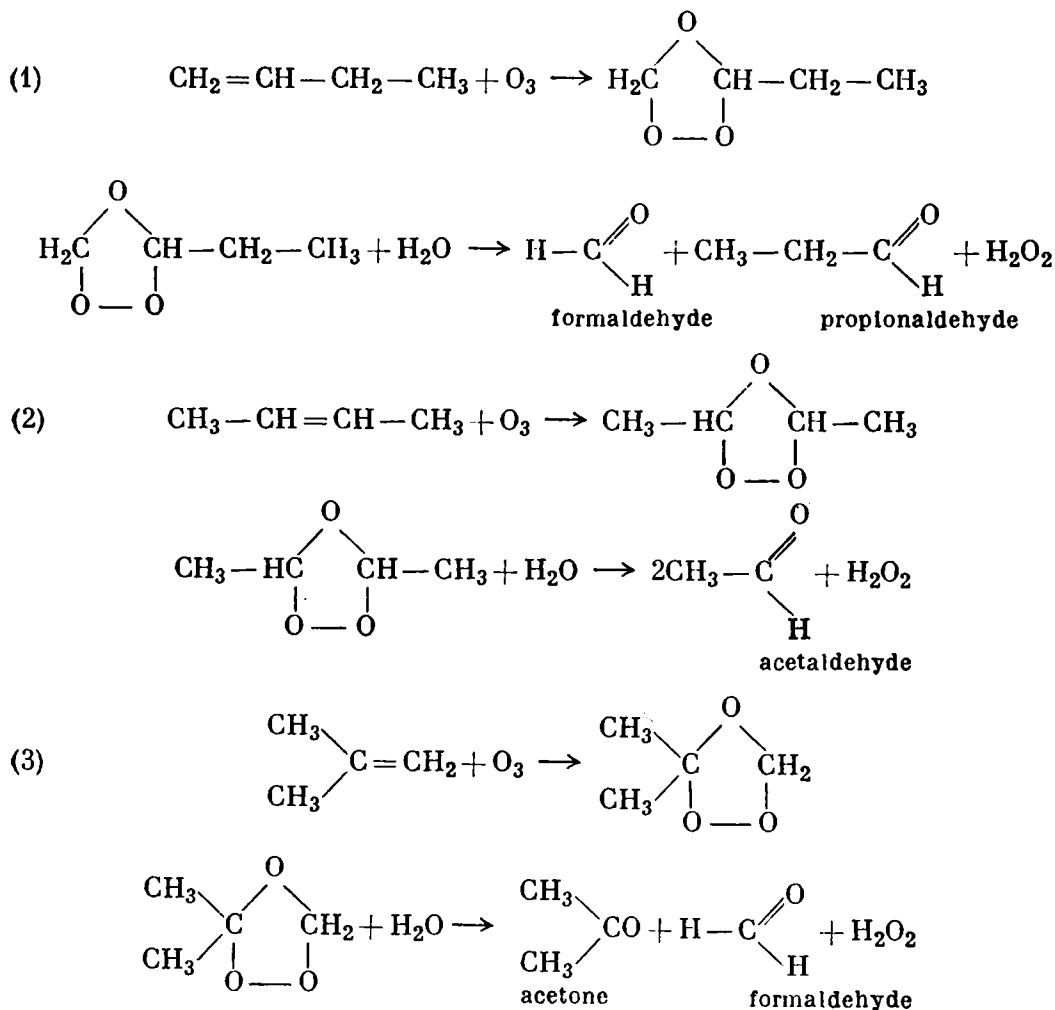


It is easy to see from these formulas that the action of ozone causes a rupture of the carbon chain. [The letters R, R', and R'' here designate various hydrocarbon radicals. For R we can substitute, say, CH₃—, and for R', C₂H₅—; or for R we can substitute C₃H₇—, and for R'', C₅H₁₁—; this will not affect the character of the reaction. In the subsequent exposition there will be frequent recourse to this generalized way of writing chemical formulas.]

The action of water causes ozonides to dissociate, with the formation of hydrogen peroxide and aldehydes or ketones:

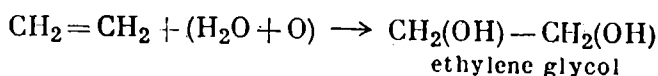


If the doubly bound carbon in the ozonized molecule had hydrogen attached to it, an aldehyde is formed; if the carbon had no hydrogen attached, a ketone is formed. Since the molecule breaks at the point where the double bond is situated, identification of the oxidation products makes it possible to determine the location of this bond. The oxidation of the three isomeric butenes provides an illustration of this:



It is evident from the above that oxidation in the first case yields formaldehyde and propionaldehyde, in the second case, acetaldehyde, and in the third, acetone and formaldehyde.

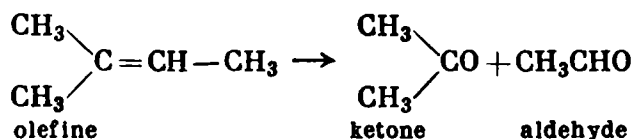
7. When olefines are oxidized carefully with a potassium permanganate solution in water, oxygen and water are added at the double bond:



The resulting products are *glycols*: i.e., alcohols with two hydroxyls in the molecule.

This reaction was discovered by Y. Wagner.

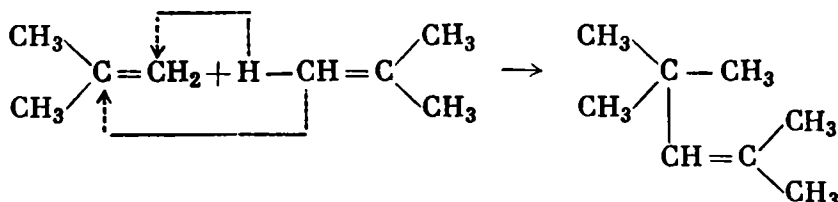
More intense oxidation splits the olefine molecule at the double bond:



8. The molecules of one and the same olefine can combine. For instance, butylene C_4H_8 forms the hydrocarbons C_8H_{16} , $\text{C}_{12}\text{H}_{24}$, etc.

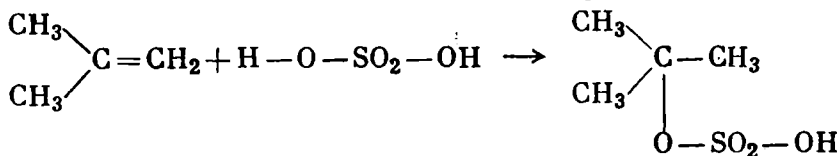
The process of the combination of several identical molecules to form a more complex one is called *polymerization*, while the substance formed is called a *polymer*.

When two identical molecules combine, we obtain a *dimer* of the initial substance:

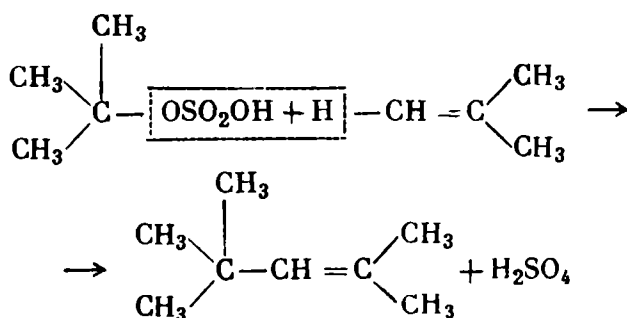


One hydrocarbon molecule is added to another at the double bond in such a way that the hydrogen atom is added to the most hydrogenated carbon atom, while the rest of the molecule is attached to the other carbon atom.

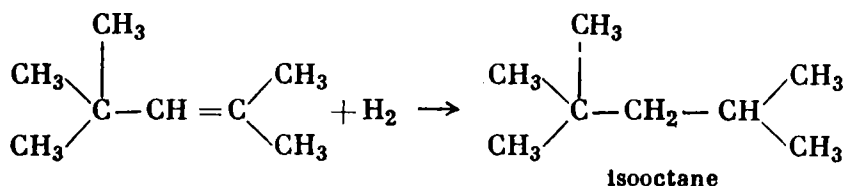
This reaction proceeds in the presence of sulphuric acid, zinc chloride, and other substances. In the case of sulphuric acid, butylsulphuric acid is formed as an intermediate product:



It then reacts with another hydrocarbon molecule:



Isobutylene (2-methylpropene) is found in petroleum cracking gases. The dimer prepared by isobutylene polymerization is converted by the action of hydrogen in the presence of catalysts into 2,2,4-trimethylpentane, which is known by the commercial name of *isooctane*:



Isooctane is an industrial product of great economic value, since it is used as an addition to gasoline for obtaining high-grade (so-called high-octane) motor fuel for internal combustion engines.

In the cylinders of internal combustion engines there is a possibility of detonation: the premature instantaneous decomposition of the petrol molecules during the moment of compression, i.e., before the piston reaches the lower dead point. Detonation, unlike normal ignition, is caused not by an electric spark from the engine spark plug, but merely by the high temperature due to the intense compression of the gas mixture by the engine piston. In the event of detonation the petrol vapours do not burn up completely, carbon monoxide and hydrogen are generated, smoke is formed, and there is a characteristic knock in the engine. This causes premature wear of the engine, while intense detonation may even ruin it altogether. The less the tendency of a petrol to detonate, the more a combustible mixture can be compressed by the piston, which means a higher engine power and more economic fuel consumption. The "anti-knocking properties" of a petrol are estimated by testing in special engines with a variable degree of compression and are expressed in units called *octane numbers*. The octane number of isooctane has been fixed at 100; normal heptane, at 0; the octane number of a mixture consisting of 80% isooctane and 20% *n*-heptane is equal to 80, etc. The "anti-knocking properties" of such mixtures serve as a standard for the petrol under investigation; its quality is characterized by an octane number corresponding to the percentage of isooctane in a mixture with *n*-heptane that has the same "anti-knocking properties". If, for instance, the mixture contains 85% isooctane, it is assumed that the octane number of the fuel is 85. When the octane number of a petrol exceeds 100, say equals 115, this means that 15% of *n*-heptane has to be added to it to obtain a petrol with the octane number 100.

The higher the octane number of an internal combustion engine fuel, the better it is. The addition of isooctane to gasoline increases engine power and reduces petrol consumption. The octane number of a petrol may also be increased by adding small quantities of so-called "anti-knock dopes", such as tetraethyllead (p. 118).

The problem of high-octane fuel was especially important in aviation before the advent of the jet engine, but it is still a major problem in relation to piston aircraft and internal combustion motor-car engines.

The octane number depends on the structure of a hydrocarbon. For normal-chain paraffins it is lower than for corresponding branched-chain paraffins, for olefines, or for cyclic hydrocarbons. For example, the octane number of *n*-hexane is 40, whereas for its isomers 3-methylpentane and 2,2-dimethylbutane it is 80 and 120 respectively; the octane number of cyclohexane is 80 and of

benzene 100. A mixture of isooctane with gasolene and neohexane (2,2-dimethylbutane) has an octane number of 115 (the octane number of straight-run gasolene is 40-60).

The double bond is the most reactive point of the molecule; it is at this point that the action of reagents is directed first and foremost.

The following qualitative reaction is highly characteristic of unsaturated hydrocarbons: a drop of bromine, when added to an olefine, at once loses its colour. Bromine water similarly loses its colour rapidly when shaken with substances whose molecules contain double bonds. *Bromine is thus a reagent for identifying the carbon double bond.* Another reagent for identifying the carbon double bond is a dilute solution of potassium permanganate and soda. When this solution is shaken with unsaturated compounds, it very quickly loses its colour and brown flakes of hydrated manganese dioxide are formed (Y. Wagner). It should, of course, be borne in mind that there are substances with carbon double bonds that are readily oxidized and that discolour potassium permanganate (e.g., aldehydes and alcohols).

32. Index of Refraction. Molecular Refraction. The index of light refraction is a very significant characteristic of liquid substances.

It will be remembered that the refractive index is the ratio of the sine of the angle of incidence (α) of the ray to the sine of the angle of refraction (β) (Fig. 13):

$$n = \frac{\sin \alpha}{\sin \beta}$$

For light of one and the same wavelength at a given temperature its value is constant and does not depend on the angle of incidence. As a rule, the refractive index of a substance diminishes with a rise in temperature and an increase in wavelength (from violet to red). Therefore it is always necessary to indicate the temperature of the experiment and the wavelength of the light. The latter is given either in millimicrons ($m\mu$), or in Ångström units Å (0.1 $m\mu$), or in letters indicating solar spectrum line wavelength:

H_{α} (red line of hydrogen spectrum)	656 $m\mu$
D (yellow line of sodium spectrum)	589 $m\mu$
H_{β} (blue line of hydrogen spectrum)	486 $m\mu$

In the chemical laboratory the index of refraction is usually determined by the Abbé refractometer (Fig. 14). When illuminated by ordinary daylight, they give the index of refraction corresponding to the D wave of the sodium (yellow) spectrum. The determinations are in most cases carried out at 20°. This being so, the index of refraction is denoted as n_D^{20} or n_{589}^{20} .

Two or three drops of a liquid are enough for a very accurate determination of the refractive index by means of a refractometer.

The index of refraction depends markedly upon the composition of a substance and its chemical structure.

Listed below, as examples, are the values of n_D^{20} for several compounds:

$n\text{-C}_4\text{H}_9\text{Cl}$	1.4015
$n\text{-C}_4\text{H}_9\text{Br}$	1.4398
$n\text{-C}_4\text{H}_9\text{I}$	1.4998
$(\text{C}_2\text{H}_5)_2\text{O}$	1.3497
$n\text{-C}_4\text{H}_9\text{OH}$	1.3991

This physical constant thus makes it possible to characterize and determine the purity of organic substances and in many cases to determine the composition of mixtures of two substances whose refractive indices differ appreciably.

It is often very useful in chemical research to employ a complex physical constant that links the refractive index n , the density d , and the molecular weight M in a general formula. This is known as the *molecular refraction* MR :

$$MR = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

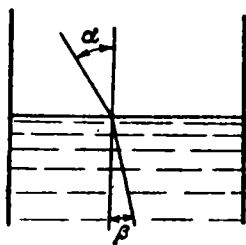


Fig. 13. Refraction of a ray at the boundary of two transparent substances.

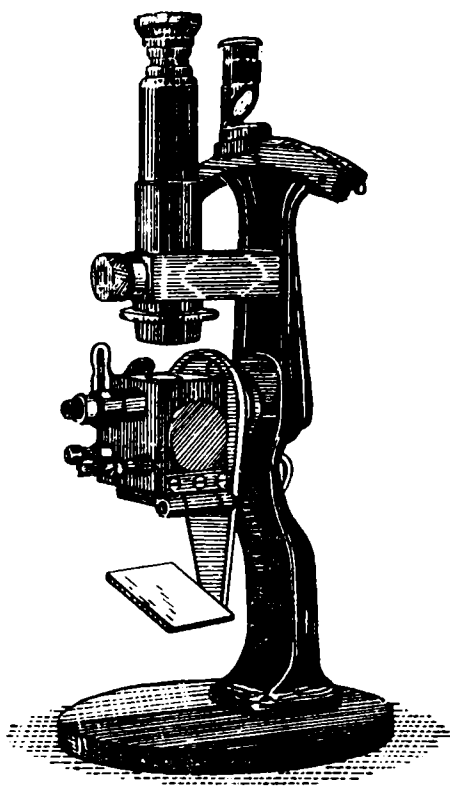


Fig. 14. A refractometer.

The molecular refraction of a substance is a constant dependent only very slightly upon temperature, since n and d change in opposite directions with temperature, the change in one balancing the change in the other.

It is essential that n and d be determined at the same temperature. The symbol MR_D indicates that n has been determined for the D line of the spectrum.

Molecular refraction depends on the nature of a substance, i.e., on its composition and chemical structure. Its value may be determined practically for a substance under investigation, provided n and d are known; besides this, it may be derived from the sum of what are known as atomic refractions, which are estimated by investigating the molecular refraction of pure substances of known composition and structure.

Here is an example of how atomic refraction values may be found. In series of homologous compounds, e.g., in the homologous series of saturated hydrocarbons, the molecular refraction increases by approximately the same value from one member of the series to the next. This value, as the average of many determinations, is equal to 4.618 (for the D line of the solar spectrum). It is evidently the refraction of the CH_2 group.

The molecular refraction of n -heptane C_7H_{16} is 34.526. Let us compute from this the atomic refraction of hydrogen and carbon:

$$4.618 \times 7 = 32.326$$

$$34.526 - 32.326 = 2.200$$

Consequently, the atomic refraction of hydrogen is 1.109, while the atomic refraction of carbon is $4.618 - 2.200 = 2.418$.

The atomic refraction of other elements may be found in the same way. For oxygen it turns out that the atomic refraction depends on whether the oxygen is in a $\text{C}=\text{O}$ group (carbonyl oxygen), a $\text{C}-\text{OH}$ group (hydroxylic oxygen), or a $\text{C}-\text{O}-\text{C}$ group (ether oxygen).

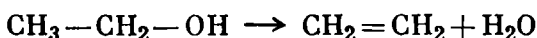
Listed below are the atomic refraction values of some of the elements (mean values of many determinations):

Sodium D line		Sodium D line	
Carbon	2.418	Chlorine	5.967
Hydrogen	1.100	Bromine	8.865
Oxygen		Iodine	13.900
carbonyl	2.211	Increment	
hydroxylic	1.643	$\text{C}=\text{C}$ double bond . .	1.733
ether	1.525	$\text{C}\equiv\text{C}$ triple bond . .	2.398

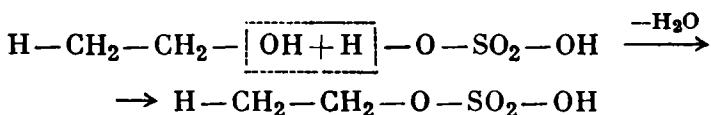
In the case of unsaturated compounds the experimentally determined molecular refraction is always greater than the atomic refraction sum. The molecular refraction of amylene C_5H_{10} , for instance, equals 24.83, whereas calculation yields the value of 23.09. The increase in molecular refraction due to the carbon double bond is called the *double bond increment*. A triple bond produces an even more pronounced exaltation of molecular refraction. The atomic refraction of carbon thus depends on the degree of its saturation.

The determination of molecular refraction plays a very important part in the identification of substances. It is at the same time a means of verifying the correctness of a structural formula: when the molecular refraction computed on the basis of the structural formula, i.e., as the sum of the atomic refractions and increments, coincides (sometimes approximately) with the experimentally found molecular refraction value, this lends weighty support to the correctness of the assumed structure.

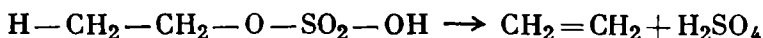
33. Ethylene. Ethylene C_2H_4 is contained in coke oven gas and in oil cracking gases. In the laboratory it is prepared by removing the elements of water from ethyl alcohol by means of concentrated sulphuric acid:



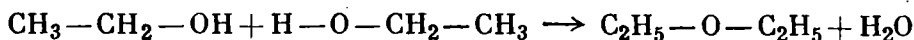
A mixture of alcohol and concentrated sulphuric acid is heated for this purpose. This first leads to the formation of ethyl hydrogen sulphate



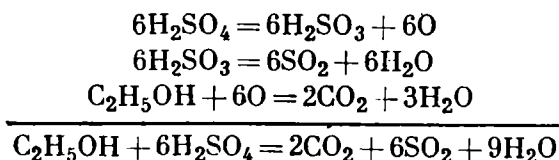
which upon further heating breaks up into ethylene and sulphuric acid:



Other products are formed at the same time. This is due to the fact that several parallel reactions proceed when sulphuric acid is heated with alcohol. For example, parallel with the removal of one molecule of water from one molecule of alcohol (forming ethylene), another molecule of water is removed from two molecules of alcohol, which results in the formation of an ether:



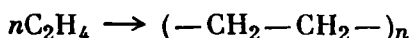
Finally, sulphuric acid, by giving up one atom of oxygen, can oxidize the alcohol, burning it to carbon dioxide and water. The sulphuric acid itself is reduced to sulphurous acid; this, being unstable, breaks up into sulphur dioxide and water:



The interaction of sulphuric acid and alcohol thus yields not only ethylene, but also ether, sulphur dioxide, and carbon dioxide.

This example shows that there can be several different reactions between an organic substance and another organic or an inorganic substance. These reactions can yield totally different products. By choosing the conditions of the reaction accordingly (temperature, pressure, the relative quantities of the substances taken, catalysts, etc.), we can make one of these reactions preponderate over the others. For example, at 170° the ethyl hydrogen sulphate decomposes forming ethylene, while at 140° it reacts with ethyl alcohol to form ether (p. 168).

Ethylene is a gas, which condenses into a liquid at -103.7° ; at -169.2° it solidifies. It is practically insoluble in water and burns with a brighter flame than methane does; with air it forms an explosive mixture. Ethylene is capable of polymerization. Its polymerization product is called *polyethylene* (*polythene*). Low- or high-molecular products are obtained depending on polymerization conditions. Polymerization at a high pressure (1,200-1,500 atm) and a high temperature yields a solid industrially valuable high-molecular product:



where n is the degree of polymerization (n can have the value of 1,000 and more).

High-molecular polythene is a yellowish-white light, horny, plastic, frost-resistant substance. It is unaffected by strong acids, including hydrofluoric acid, or alkalis.

Complex organometallic catalysts discovered in recent years have made it possible to prepare high-molecular solid polymers of ethylene (polythene) without resorting to pressure. One such extensively employed catalyst is a system consisting of $Al(C_2H_5)_3$ and titanium tetrachloride $TiCl_4$. The reaction between these two compounds produces a solid substance, which consists of a complicated organometallic complex that has a catalytic effect on the polymerization of ethylene. The polythene produced by means of this catalyst is a saturated hydrocarbon of normal structure. It is less elastic than the polythene produced at high pressures, but is harder and can withstand higher temperatures.

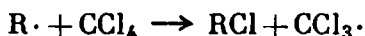
Combining as it does many valuable properties, polythene has very many applications. It is one of the finest materials for insulating cable, for use in radar, radio, and television equipment, etc. Pipes, flexible hosing, vessels, films of varying thickness, and many household goods are made out of it.

In addition to this, ethylene is used to produce the highly important semi-manufactures basic to the production of such synthetic materials as styrene, ethylene oxide, and vinyl chloride. It serves to make ethyl alcohol and several valuable solvents, while the treat-

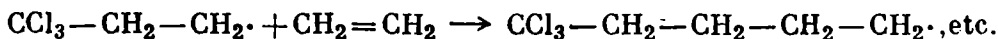
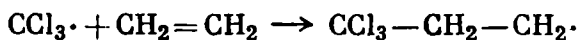
ment of sulphur chloride with ethylene produces the war gas yperite, or mustard gas (p. 174).

It has been found that if green tomatoes, plucked before they are ripe, are exposed to an atmosphere of ethylene, their ripening is considerably accelerated, even when the ethylene content in the air is negligible. Ethylene is now used on a large scale to hasten the ripening of fruit.

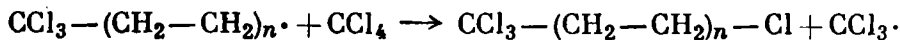
Telomerization. An interesting process of ethylene polymerization recently discovered and now employed industrially is called telomerization. If benzoyl peroxide or some other initiating agent, which breaks up the free radicals formed, is introduced into a mixture of ethylene and CCl_4 , the following process takes place:



The $\text{CCl}_3\cdot$ radicals initiate the chain polymerization of ethylene:



The growth of the chain ceases when another CCl_4 molecule is encountered:



The $\text{CCl}_3\cdot$ radical gives rise to a new chain.

The resulting low-molecular polymerization products, which have residues of the solvent molecule at the ends, are called *telomers*. Telomers have been prepared with the values of $n = 2, 3, 4, \dots 15$. By hydrolysis or ammonolysis telomers can be converted to oxy and amino acids:



34. Isobutylene. Isobutylene $\text{CH}_2=\text{C}(\text{CH}_3)_2$ is a colourless gas (b.p. -69°) obtained from petroleum refining gases. It was first synthesized by Butlerov in 1868. Under the influence of zinc chloride, boron trifluoride, aluminium chloride, and other catalysts, isobutylene polymerizes. Depending on the conditions of polymerization, we obtain polymers of different molecular weight, ranging from viscous liquids to solid elastic materials. A material that has acquired industrial use is *polyisobutylene* (*oppanol*), a high-molecular solid polymer with an average molecular weight of from 100,000 to 500,000. It is chemically- and water-resistant, and is used as a corrosion-resistant liner and protective film.

Especially important industrially is the copolymer of isobutylene with 2-3% of isoprene, which is known as *butyl rubber* (p. 94). Butyl rubber is gas-proof and is, accordingly, used for the inner tubes of car tyres, for the inner layer of tubeless tyres, and various other rubber goods.

Hydrocarbons with a Triple Bond

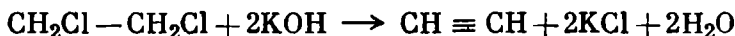
35. Structure of Acetylene Hydrocarbons and Their Preparation. The simplest hydrocarbon with a triple bond is acetylene C_2H_2 , or $H-C \equiv C-H$.

The other members of the homologous series of hydrocarbons with one triple bond in the molecule are derived from acetylene by the substitution of alkyls for the hydrogen atoms in its molecule. Their names, in accordance with the Geneva system, have the ending *yne*:

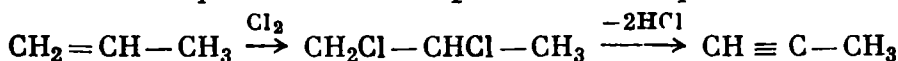
acetylene—ethyne	$CH \equiv CH$
methylacetylene—propyne	$CH \equiv C-CH_3$
ethylacetylene—butyne-1	$CH \equiv C-CH_2-CH_3$
dimethylacetylene—butyne-2	$CH_3-C \equiv C-CH_3$, etc.

Since the molecules of the acetylene hydrocarbons with one triple bond contain four hydrogen atoms less than the molecules of corresponding saturated hydrocarbons, their composition can be expressed by the general formula C_nH_{2n-2} .

Acetylene hydrocarbons are formed in the dry distillation of many organic substances. They can be obtained, as shown by Savich in 1861, by removing two hydrogen halide molecules from compounds containing two halogen atoms attached to neighbouring carbon atoms:



Since such halogen compounds are obtained by the addition of halogens to olefines, the above reaction makes it possible to convert double bond compounds into triple bond compounds:



The acetylene hydrocarbons have been studied by many chemists. Work of particular importance has been done in this field by the schools of A. Favorsky* and N. Zelinsky, which enjoy world-wide reputations.

* Alexei Favorsky (1860-1945) was an outstanding pupil of Butlerov.

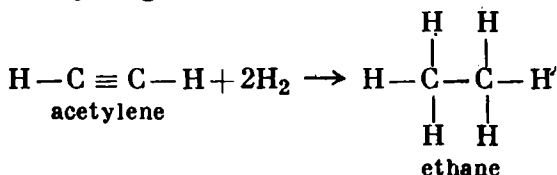
He did extensive research in the acetylene hydrocarbons and products prepared on the basis of acetylene. Favorsky discovered and investigated the phenomena of the isomerism and mutual transition of acetylene and allene hydrocarbons. He evolved a technique of preparing vinyl ethers by treating acetylene with alcohols in the presence of powdered potassium hydroxide. With his pupils, he later elaborated upon this reaction and worked out industrial methods for producing vinyl ethers (M. Shostakovsky). The reactions of acetylene and acetylene hydrocarbons with ketones, which were proposed by Favorsky and his pupils (I. Nazarov), have been put to extensive practical use. Isoprene for synthetic rubber can be produced by this method.

In 1902 Favorsky took over the chair of organic chemistry at the University of St. Petersburg. In 1929 he was elected a member of the Academy of Sciences of the U.S.S.R. His pupils included many outstanding chemists (S. Lebedev, B. Byzov, I. Nazarov, and others).

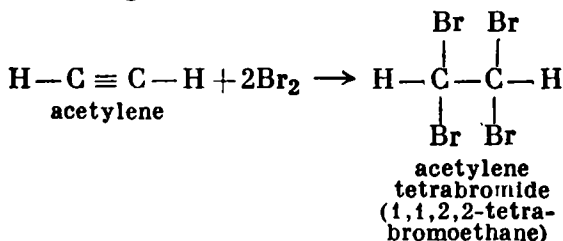
36. Properties of Acetylene Hydrocarbons. Acetylene and methylacetylene are gases, the homologues that follow are liquids, and the highest members of the series are solids. Acetylene hydrocarbons have higher boiling points than the corresponding saturated hydrocarbons. For instance, while the boiling point of *n*-pentane is 36°, the boiling point of pentyne-1 is 39.7°.

The acetylene hydrocarbons are still less saturated than the ethylene hydrocarbons. For this reason they readily react additively. Their molecules are capable of adding four atoms of hydrogen or a halogen, or, alternatively, two molecules of a hydrogen halide.

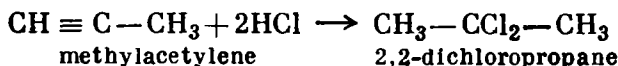
1. Addition of hydrogen:



2. Addition of halogens:



3. The addition of hydrogen halides takes place in accordance with Markovnikov's rule:

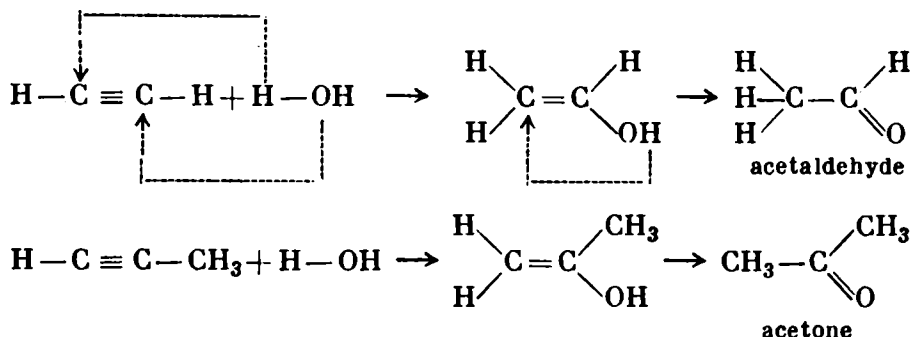


4. When acetylene is released into water containing a mercuric salt and sulphuric acid as a catalyst, the acetylene molecule adds a molecule of water, forming acetaldehyde. This reaction, discovered by M. Kucherov* in 1881, nowadays serves for the industrial manufacture of acetaldehyde, which is then oxidized to acetic acid. The homologues of acetylene in these conditions yield ketones.

* Mikhail Kucherov (1850-1911) was Professor at the St. Petersburg Institute of Agriculture. He began investigating the hydration of acetylene in 1875 or thereabouts. The reaction producing acetaldehyde was discovered by him in 1881.

By his subsequent research Kucherov demonstrated that methylacetylene and phenylacetylene react analogously, yielding not aldehydes, but, as might have been expected, ketones. He also studied the interaction of olefines with salts of mercury.

The reaction may be represented as follows:

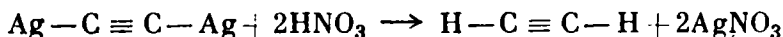


An unsaturated alcohol is formed at first; however, as demonstrated by A. Eltekov, compounds containing a hydroxyl attached to a doubly bound carbon atom undergo isomerization to form aldehydes or ketones.

5. Acetylene hydrocarbons are readily oxidized by oxidizing agents. Vigorous oxidation causes a rupture of the carbon chain at the point of the triple bond.

6. If a triply bound carbon atom in an acetylene hydrocarbon has a hydrogen atom attached to it, the hydrogen atom may be replaced by a metal. When, for example, acetylene is passed through ammoniacal silver nitrate, a white precipitate of silver acetylide $\text{Ag}-\text{C}\equiv\text{C}-\text{Ag}$ is formed. An ammoniacal solution of copper chloride produces a reddish-brown precipitate of cuprous acetylide. Dry cuprous and silver acetylides are highly explosive; they explode if heated or struck.

The action of acids upon the metal acetylides results in the regeneration of acetylene:

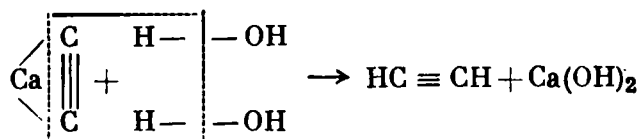


7. Acetylene hydrocarbons are capable of polymerization. In the presence of cuprous salts (catalyst) acetylene is thus polymerized into a highly interesting product: vinylacetylene $\text{CH}\equiv\text{C}-\text{CH}=\text{CH}_2$. It can be looked upon as the product of the substitution of the vinyl radical $-\text{CH}=\text{CH}_2$ for a hydrogen atom in acetylene.

Vinylacetylene is an intermediate product in the manufacture of one of the types of synthetic rubber (p. 101). It boils at 5° .

37. Acetylene. Acetylene is formed in the dry distillation of many organic substances. The synthesis of acetylene from its elements (the formation of acetylene in a voltaic arc between carbon electrodes in a hydrogen atmosphere), achieved by Berthelot in 1860, was the first synthesis of a simple hydrocarbon.

Until recently acetylene was prepared only by the action of water upon calcium carbide:



This reaction was discovered by Wöhler in 1852, but it acquired practical importance only when a technique was developed for obtaining calcium carbide by heating lime and coke in an electric furnace. Acetylene production from petroleum crudes and natural gases is becoming highly important today. The methane in these raw materials is converted to acetylene under the very brief (hundredths of a second) effect of very high temperatures (1400° and higher):



The reaction is highly endothermic, and the industrial methods of acetylene production differ according to the technique whereby the heat is supplied (voltaic arc, the burning of part of the methane directly in the reaction vessel, etc.). In the same way, but at a somewhat lower temperatures, acetylene can be produced from higher hydrocarbons (propane, butane, or the light petroleum cuts). The reaction of acetylene production from hydrocarbons proceeds in a complicated manner and is accompanied by the formation of a large number of by-products: ethylene, carbon in the form of carbon black, and acetylene homologues. The methods developed for separating the gas mixture into its individual components, with subsequent thorough purification, make it possible to isolate the acetylene in sufficiently pure form.

Acetylene is a colourless gas; when absolutely pure, it has a slight ether-like odour. As prepared from carbide and not purified, it has an unpleasant odour, due to phosphine and hydrogen sulphide impurities. The solubility of acetylene in water is relatively high; it is quite easily condensed into a liquid, which boils at -83.6° .

Since acetylene contains a higher percentage of carbon than either ethylene or methane, it burns with a more luminous and smokier flame. When, however, it is mixed with a large amount of air, which is effected by special acetylene burners, its flame is bright and not smoky.

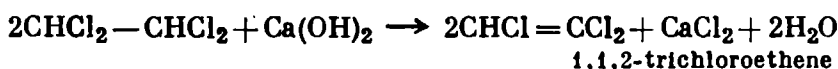
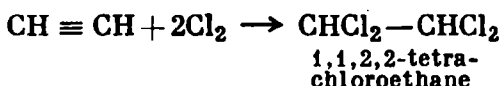
The temperature produced by the burning of acetylene, especially in oxygen, is very high (even higher than when hydrogen is burned); for this reason the oxyacetylene torch is used extensively for welding and cutting metals.

Compressed, and especially liquid, acetylene is apt to explode at the slightest shock. This being so, it is stored and transported in

steel tanks in which it is dissolved in acetone under pressure. The explosive properties of acetylene are due to the fact that it is an endothermic substance, i.e., its burning produces more heat than the burning of an equivalent amount of carbon and hydrogen. 54.8 Cal per mol are generated when acetylene is decomposed into carbon and hydrogen.

With air acetylene forms extremely explosive mixtures; such mixtures are apt to explode unless the acetylene forms less than 3% or more than 82% of the mixture.

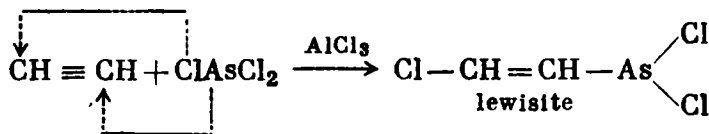
Acetylene is used on an enormous scale as a material for preparing a number of chemical compounds. The Kucherov reaction converts acetylene into acetaldehyde, which in turn is used to prepare acetic acid and other compounds. Two excellent solvents for fats and sulphur are obtained from acetylene: *tetrachloroethane* $\text{CHCl}_2-\text{CHCl}_2$ and *trichloroethene* $\text{CHCl}=\text{CCl}_2$ (the latter is prepared by boiling tetrachloroethane with lime)



Unlike many other solvents, they are almost nonflammable and do not therefore create a fire hazard. They are used for degreasing and for rubber vulcanization.

Very considerable quantities of acetylene are used for the synthesis of rubber (p. 97 fol.) and the preparation of polyvinyl chloride plastics (p. 113).

When acetylene is passed through arsenic trichloride AsCl_3 in the presence of aluminium chloride AlCl_3 (which acts as a catalyst), chlorovinylchloroarsine is formed:



This substance was manufactured during the First World War as a chemical warfare agent and was named lewisite.

Lewisite is a liquid having a geranium odour. Like yperite, it is a vesicant producing blisters; apart from this, it is a generally toxic and irritant agent.

Hydrocarbons with Two Double Bonds. Rubber

38. Structure and Properties of Hydrocarbons with Two Double Bonds. Insofar as every double bond reduces the amount of hydrogen in a molecule by two atoms, while a triple bond reduces it by four atoms, hydrocarbons with two double bonds have the same composi-

This is illustrated by the case of the two isomers of hexadiene (C_6H_{10} , molecular weight 82.16).

(a) Hexadiene-1,5 with two isolated double bonds has the following refractive index and density:

$$n_D^{20} = 1.4044; \quad d_4^{20} = 0.6880$$

Its molecular refraction is:

$$MR_D = \frac{1.4044^2 - 1}{1.4044^2 + 2} \cdot \frac{82.16}{0.6880} = 29.12$$

(b) Hexadiene-1,3 with a system of two conjugated double bonds has the following refractive index and relative density:

$$n_D^{20} = 1.4384; \quad d_4^{20} = 0.7108$$

Its molecular refraction is:

$$MR_D = \frac{1.4384^2 - 1}{1.4384^2 + 2} \cdot \frac{82.16}{0.7108} = 30.36$$

Now let us compute the molecular refraction MR_D from the atomic refractions:

$$\begin{array}{rcl} C_6 & 2.418 \times 6 & = 14.508 \\ H_{10} & 1.100 \times 10 & = 11.000 \\ & 1.733 \times 2 & = 3.466 \\ & \hline & & 28.974 \end{array}$$

For the isomer with the isolated double bonds the discrepancy between the experimental value of the molecular refraction and the computed value is 0.15, whereas for the isomer with the conjugated double bonds this discrepancy is 1.39.

This rise, or *exaltation*, of the molecular refraction is observed regularly in compounds with conjugated double bonds.

In this way the value of the molecular refraction can in a number of cases provide a clue to the structure of an unsaturated hydrocarbon.

For a discussion of present-day concepts of the structure of the double bond and the phenomena of conjugation see pp. 226-31.

39. Rubber and Its Properties. Natural rubber, or caoutchouc, in the purified state is a polymer whose general formula is $(C_5H_8)_x$. It is obtained mainly from the milky fluid, called latex, of certain tropical plants, primarily the huge tree *Hevea brasiliensis*.

The Indians of South America called this milky liquid "caa-o-choo", meaning "the tree's tears".

French scientists who studied the properties of the substance gave it the name caoutchouc.

In the latex the caoutchouc or natural rubber is in colloid form. The addition of a small amount of acetic acid causes it to coagulate

into a coherent mass and separate from the liquid. The coagulum is pressed between rollers into sheets and is then dried and smoked to prevent mouldiness and deterioration.

Rubber is highly soluble in petrol, benzene, and carbon disulphide. At a low temperature it becomes brittle; upon heating, sticky. To improve its mechanical and chemical properties, it is turned into *vulcanized rubber*. In the manufacture of rubber articles they are first moulded of a mixture of rubber with sulphur, as well as with so-called fillers (carbon black, chalk, clay, and certain organic substances, which serve to accelerate vulcanization) and then heated. This is known as *hot vulcanization*.

In *cold vulcanization*, which is used for small and thin articles (rubberized tissues, thin tubes, etc.), the articles are subjected to brief treatment with a solution of sulphur in carbon disulphide or sulphur chloride. Rubber with a high sulphur content (up to 32%) is a solid inelastic substance called *ebonite*; it is used as an insulator in electric appliances.

Vulcanization binds the sulphur chemically with the rubber. Besides this, vulcanized rubber contains tiny particles of free sulphur.

Technical progress and the increased use of motors in the national economy make rubber a material of prime importance. It has a tremendous number of applications: it is used to manufacture tyres for motor-cars, bicycles, and aircraft, train brake hose, rubberized transmission belts, insulation for electric wires, gas masks, tractor and car valves, galoshes, various household and medical articles, certain laboratory equipment*, etc.

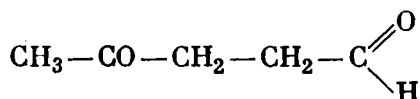
The world's rubber production in 1916 amounted to 200,000 tons; by the beginning of the Second World War it had reached about 1 million tons. The bulk of the natural rubber comes from the plantations in South-East Asian countries.

40. Structure and Synthesis of Rubber. Chemically it is a high-molecular unsaturated hydrocarbon, a mixture of complicated polymer molecules. As an unsaturated compound rubber reacts additively with bromine and the hydrogen halides, one C_5H_8 group adding two bromine atoms or one hydrogen halide molecule. Consequently, there is one double bond to every C_5H_8 group in the

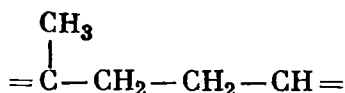
* In the chemical laboratory extensive use is made of rubber stoppers and tubes of varying diameter to connect parts of apparatus and supply water and gas. When working with them, it is necessary to bear in mind the properties of rubber. Rubber has a high resistance to the action of dilute alkalis and dilute hydrochloric acid, but is easily ruined by concentrated sulphuric acid and, especially, concentrated nitric acid. Organic solvents (e.g., halogen derivatives of hydrocarbons) cause rubber to swell and dissolve. Chlorine or bromine vapours make it hard and brittle.

rubber molecule. One of the hydrocarbons formed in the dry distillation of rubber is isoprene C_5H_8 .

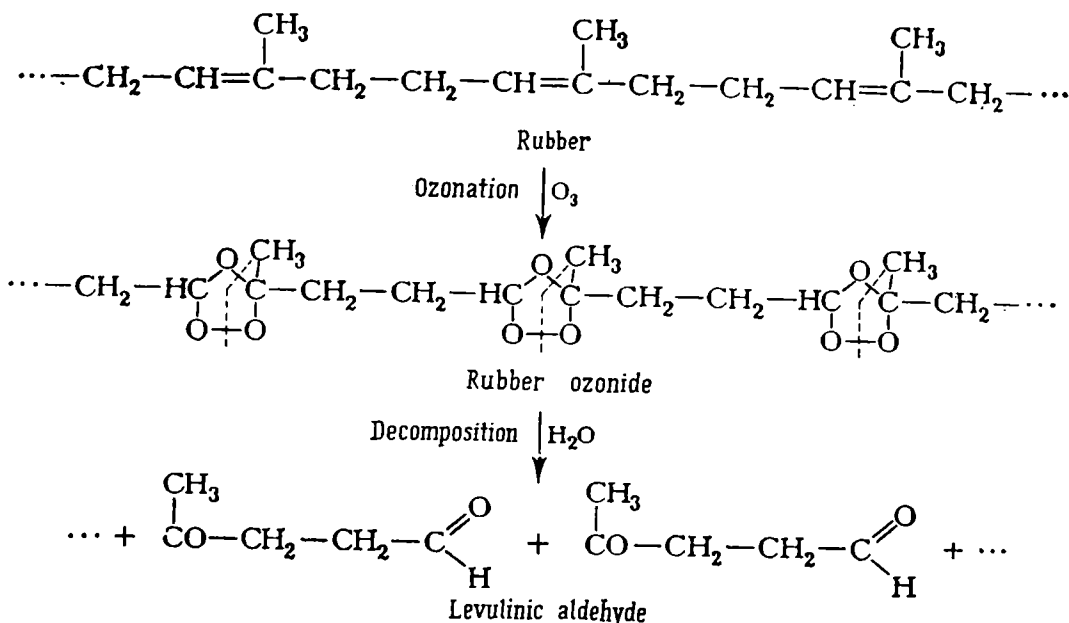
The first information about the structure of rubber was obtained in 1905, when C. Harries treated rubber with ozone and obtained a vitreous ozonide of the composition $C_{10}H_{16}O_6$. When this ozonide is decomposed by water, the product contains up to 90% of levulinic aldehyde:



The fact that this compound is formed in the decomposition of the ozonide indicates that the rubber molecule contains the regularly recurring group

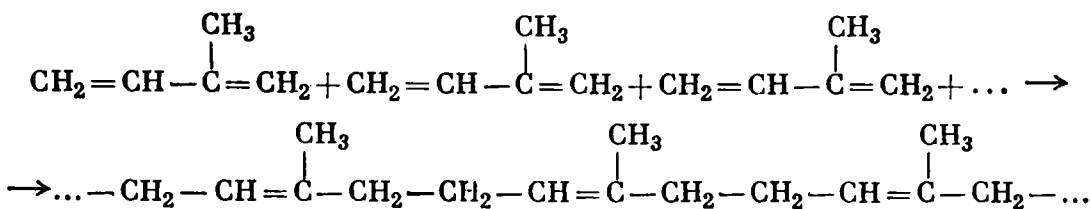


i.e., that in the rubber molecule there is a sequence of isoprene groups:



To derive the formula of rubber we may assume that the isoprene molecules interact with one another as systems with conjugated bonds, i.e., that addition takes place at the ends of the chain, while between the middle carbon atoms there arises a double bond (in

accordance with Thiele's rule):



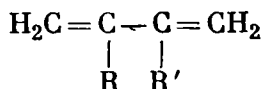
The composition of the groups at the ends of the chain is still not clear.

Natural rubber is a typical example of a high-molecular compound. Staudinger, by determining the viscosity of rubber solutions, established that caoutchouc from the *Hevea* has a molecular weight of approximately 170,000, which corresponds to 2,500 isoprene groups; this means that the polymerization coefficient n is equal to 2,500. When rubber is isolated from natural substances its molecular chain is ruptured and the polymerization coefficient diminishes; in the commercial product it is equal to about 400. The polymerization coefficient differs from molecule to molecule in the same rubber sample. Rubber molecules contain different numbers of isoprene groups. They are members of the polymer homologous series $(\text{C}_5\text{H}_8)_n$, differing from one another in composition by this or that number of C_5H_8 groups. This being so, it is possible to speak only of the average molecular weight.

As stated above, rubber is "vulcanized" by heating with sulphur. The mechanism of vulcanization is apparently such that the individual linear molecules of rubber become linked at various points through the sulphur atoms.

The high-molecular compounds formed have a latticed structure and are less elastic than the initial material. The greater the amount of sulphur added, the more of these connecting bridges are formed by sulphur atoms and the harder and less elastic the product becomes.

The tremendous practical importance of rubber turned chemical thought long ago to the problem of preparing it synthetically. However, the industrial synthesis of isoprene itself presented formidable difficulties. In view of this, the first attempts to obtain rubber-like products were made with isoprene analogues—hydrocarbons containing the conjugated bond system



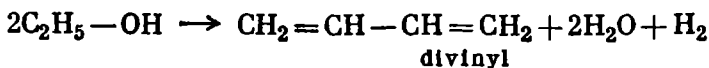
where R and R' are alkyls.

A rubber-like substance was first prepared in 1902 by I. Kondakov, who polymerized dimethylbutadiene. Later, during the First

World War, an attempt to manufacture synthetic rubber industrially from dimethylbutadiene was made in Germany; a mere 2 tons of "methyl-rubber" were made, for the product turned out to be of little value technically.

Synthetic rubber was first produced industrially in the U.S.S.R. A large share of the credit for this is due to S. Lebedev*. He proposed and developed the method of the industrial production of synthetic rubber on the basis of divinyl.

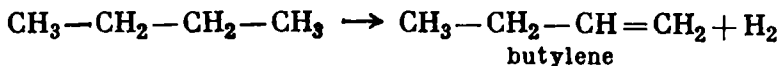
The raw material for preparing synthetic rubber according to the Lebedev method is ethyl alcohol. The passage of ethyl alcohol vapour at 400-500° over a catalyst, whose composition was developed by Lebedev, produces a mixture of substances from which divinyl can be isolated:



Divinyl separated from by-products is subjected to polymerization in the presence of metallic sodium; this yields a mass similar in properties to natural rubber, which is then vulcanized.

Today divinyl is produced not only from alcohol. The method that has proved most advantageous is that of producing it from butane, which is contained in casing-head gases, or from the butylene cut of refinery gases.

When butane, at 550-600°, is passed over a catalyst consisting of a mixture of aluminium and chromium oxides, a reaction of dehydrogenation takes place:



* Sergei Lebedev (1874-1934) was born in Lublin and received his secondary schooling in Warsaw. In 1895 he entered the Physics and Mathematics Department at the University of St. Petersburg.

Lebedev's instructor was Favorsky, who supervised his early research work. The study of the polymerization of unsaturated organic compounds was begun by Lebedev in 1906. In December, 1909, he presented a paper to the Russian Chemical Society on the polymerization of diene hydrocarbons and demonstrated a rubber-like compound prepared from divinyl.

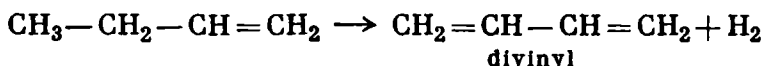
In April, 1913, Lebedev presented his M.Sc. dissertation "Investigations in the Polymerization of Diene Hydrocarbons".

In 1925 he founded the Petroleum Refining Laboratory at Leningrad University, where the preparation of synthetic rubber from alcohol (via divinyl) was accomplished.

Following this, Lebedev personally supervised the building of a pilot plant which in January, 1931, turned out the first stock of the industrial product.

In 1928 Lebedev was elected a corresponding member and in 1932 a full member of the Academy of Sciences of the U.S.S.R. For his outstanding services in solving the problem of synthetic rubber production he was decorated with the Order of Lenin.

The butylene is again dehydrogenated, at a higher temperature, over a catalyst of a different composition:

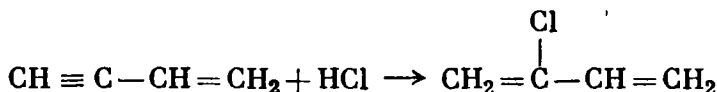


By selecting a suitable catalyst and reaction conditions, the process can be effected in a single stage:

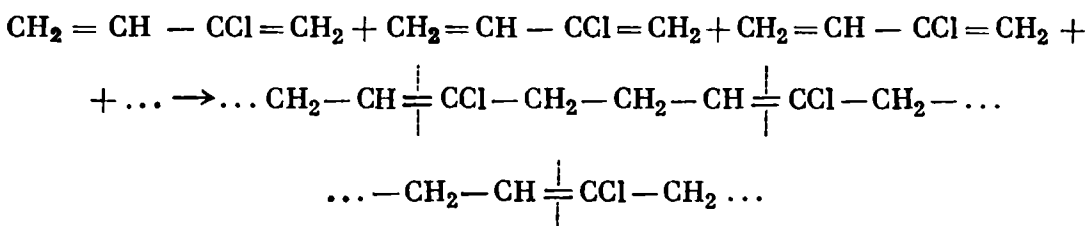


The synthesis of divinyl from petroleum hydrocarbons was first suggested by B. Byzov back in the twenties. However, the equipment in use at the time did not make it possible to isolate the individual hydrocarbons in sufficiently pure form. At present the dehydrogenation of butane and of butylenes is the most widespread method of producing divinyl in the U.S.S.R. and in most other countries.

One type of synthetic rubber is produced from acetylene. It was pointed out above (p. 91) that the polymerization of acetylene yields vinylacetylene $\text{CH}\equiv\text{C}-\text{CH}=\text{CH}_2$. Vinylacetylene adds a molecule of hydrogen chloride, forming 2-chlorobutadiene-1,3 (*chloroprene*):



Chloroprene is a colourless liquid boiling at 59°. It very readily polymerizes spontaneously, forming first a plastic resembling unvulcanized rubber and then a solid (vulcanization without sulphur):



This structure is confirmed by the fact that the oxidation of synthetic rubber of this type produces succinic acid $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{COOH}$. The points at which the carbon chain is ruptured are indicated by dotted line.

Chloroprene rubber is nonflammable, as well as resistant to heat, light, and lubricants. For this reason it is used extensively in the production of rubber goods.

Rubber has to meet the most varied requirements in industry. In some cases the need is for high resilience; in other cases, for high elasticity; in still others, for heat resistance.

Since all these requirements cannot be met by any single type of rubber, dozens of different types are produced, based on the most diverse chemical compounds. The valuable properties of the chloroprene rubbers and butyl rubber were mentioned above. The rubbers based on organosilicon compounds retain their elastic properties at both high and low temperatures; the rubbers based on organofluorine compounds combine temperature stability with an almost absolute resistance to chemical attack, and the rubbers prepared by the copolymerization of divinyl and acrylonitrile exhibit a high resistance to petrol and other petroleum products. The most widespread type of rubber, used extensively in the manufacture of tyres, is that produced by the copolymerization of divinyl and styrene (p. 446). This type of rubber is very strong and is therefore produced in enormous quantities. However, in elasticity and certain other properties it is inferior to natural rubber, which for this reason had no substitutes until recently in the manufacture of quite a few products. The valuable properties of natural rubber may be traced to the structure of the polymer chain, which is distinguished by a highly regular spatial arrangement of individual links. For a long time efforts to reproduce this structure in synthetic rubbers were unsuccessful. Only in the fifties was it discovered that polymers of regular structure can be produced by polymerization in the presence of complex organometallic catalysts.

Rubbers produced by this technique from butadiene and from isoprene are even superior to natural rubber in some properties.

The discovery of such stereospecific polymerization has given a new impetus to the production of synthetic rubber.

Various types of synthetic rubber possess specific properties far superior to the properties of natural rubber; resistance to petrol and lubricants, heat resistance, resistance to gas diffusion, opacity, resistance to chemical attack, etc. For this reason natural rubber no longer occupies the exclusive position it did half a century ago.

Halogen Derivatives of Hydrocarbons

Depending upon the number of hydrogen atoms replaced by the halogen, there may be monohalogen, dihalogen, trihalogen, and, in general, polyhalogen compounds. The halogen derivatives of methane are a case in point:

CH_3Cl
methyl
chloride

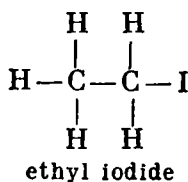
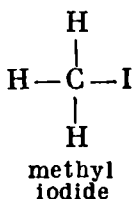
CH_2Cl_2
methylene
chloride

CHCl_3
chloroform

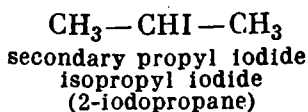
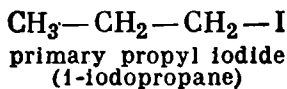
CCl_4
carbon
tetrachloride

41. Alkyl Halides. Their Isomerism and Preparation. The monohalogen derivatives of the saturated hydrocarbons are called alkyl halides; their composition may be expressed by the general formula $\text{C}_n\text{H}_{2n+1}\text{X}$, where X may be F, Cl, Br or I.

In the methane molecule all the hydrogen atoms are equivalent; the same is true of all the hydrogen atoms in the ethane molecule. Therefore, the substitution of some halogen, say iodine, for a hydrogen atom in either methane or ethane can produce only one halogen derivative in each case:



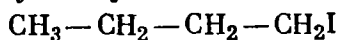
But by replacing a hydrogen atom in propane $\text{CH}_3-\text{CH}_2-\text{CH}_3$, we can derive two propyl iodides (chlorides, bromides, fluorides):



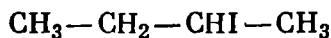
In the molecule of the first of these substances the iodine atom is attached to a primary carbon atom, while in the molecule of the second it is attached to a secondary carbon atom. Primary propyl iodide boils at 102.5° ; isopropyl iodide boils at 89.5° .

An even greater number of isomers can be derived from the butanes. By replacing a hydrogen atom in normal butane CH_3-CH_2-

—CH₂—CH₃, we obtain normal primary butyl iodide and normal secondary butyl iodide:



normal primary
butyl iodide
(1-iodobutane)



normal secondary
butyl iodide
(2-iodobutane)

When a hydrogen atom is replaced by iodine in a molecule of isobutane, two other isomers are formed: isobutyl iodide and tertiary butyl iodide:



isobutyl iodide
(1-iodo-2-methyl-
propane)



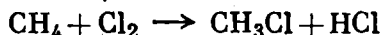
tertiary butyl iodide
(2-iodo-2-methyl-
propane)

In the molecule of the latter compound the iodine atom is attached to a tertiary carbon atom.

Four isomers are thus possible (and are, indeed, known) for the substance C₄H₉I. The same number of isomers can of course be obtained by replacing the hydrogen atom by any other halogen.

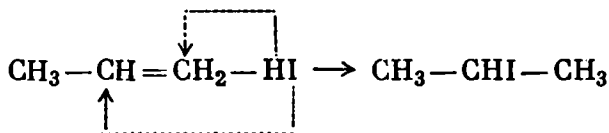
Alkyl halides can be prepared by several methods:

1. By the action of chlorine or bromine on saturated hydrocarbons:

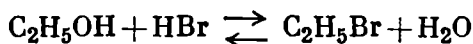


As pointed out above, the reactions of chlorination and bromination proceed under the influence of light.

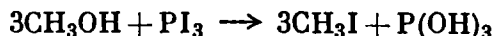
2. By the addition of hydrogen halides to olefines. This addition takes place according to Markovnikov's rule:



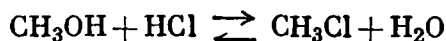
3. By the substitution of a halogen for a hydroxyl of an alcohol. This can be accomplished by the action of a concentrated halogen acid on an alcohol:



or by the interaction of alcohols with halogen compounds of phosphorus:



The reaction between an alcohol and a hydrogen halide is reversible:



To shift the balance to the right, a dehydrated alcohol is taken. The presence of strong sulphuric acid, which binds the water formed, likewise increases the alkyl halide yield (for further details see p. 135).

42. Properties of Alkyl Halides. The lowest alkyl halides are gases, the ones following are liquids, and the highest are solids.

Table 3 gives the boiling points and densities of some of the alkyl halides; the data refer to the normal primary compounds.

A glance at the horizontal lines of the table will show that the iodides have a greater density and boil at a higher temperature than corresponding bromides; similarly, the bromides have a greater density and boil at a higher temperature than the chlorides.

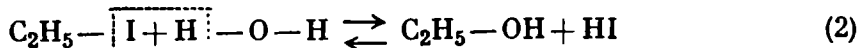
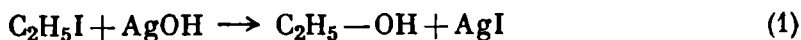
The boiling points and densities of the halogen derivatives thus rise with an increase in the atomic weight of the halogen in the molecule.

If we now compare the figures in the vertical columns of the table, we shall see that the densities of the halogen derivatives decline and the boiling points rise with the increase in the number of carbon atoms in the molecule.

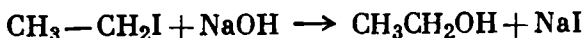
The alkyl halides are practically insoluble in water. The lowest of them have a characteristic odour and, when introduced into a flame on a copper wire, impart a green colour to it at the fringes (Beilstein test for halogens).

The alkyl halides rank among organic substances with a high reactivity: they readily exchange the halogen atom for various groups.

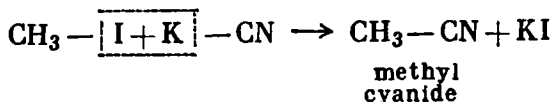
1. Under the action of silver hydroxide or even water (especially in the presence of alkaline substances) the alkyl halides yield alcohols:



Reaction (2) is reversible. For it to proceed in the direction of alcohol formation, it is necessary to take a large amount of water or else remove the halogen acid formed by distilling it off or by adding sodium hydroxide, soda or other alkalis:



2. With potassium cyanide the alkyl halides form alkyl cyanides (nitriles):



3. The action of metallic sodium on the alkyl halides produces paraffins (Wurtz reaction):

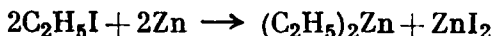


A large number of such reactions are known. For this reason the alkyl halides are of exceptional importance in synthesizing other substances.

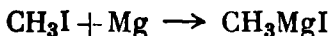
TABLE 3. Boiling Points and Densities of Some Primary Alkyl Halides
(Normal Structure)

Alkyl halide	B.p., °C	d_4^{20}	Alkyl halide	B.p., °C	d_4^{20}	Alkyl halide	B.p., °C	d_4^{20}
CH_3Cl methyl chloride	-23.7	0.952 (at 0°)	CH_3Br methyl bromide	3.5	1.732 (at 0°)	CH_3I methyl iodide	42.5	2.279
$\text{C}_2\text{H}_5\text{Cl}$ ethyl chloride	13.1	0.918 (at 8°)	$\text{C}_2\text{H}_5\text{Br}$ ethyl bromide	38.4	1.461	$\text{C}_2\text{H}_5\text{I}$ ethyl iodide	72.3	1.936
$\text{C}_3\text{H}_7\text{Cl}$ propyl chloride	46.6	0.892	$\text{C}_3\text{H}_7\text{Br}$ propyl bromide	71.0	1.351	$\text{C}_3\text{H}_7\text{I}$ propyl iodide	102.5	1.749
$\text{C}_4\text{H}_9\text{Cl}$ butyl chloride	78.5	0.887	$\text{C}_4\text{H}_9\text{Br}$ butyl bromide	101.6	1.276	$\text{C}_4\text{H}_9\text{I}$ butyl iodide	130.4	1.615
$\text{C}_5\text{H}_{11}\text{Cl}$ amyl chloride	108.4	0.878	$\text{C}_5\text{H}_{11}\text{Br}$ amyl bromide	127.9	1.218	$\text{C}_5\text{H}_{11}\text{I}$ amyl iodide	154.2	1.510

4. The action of zinc on the alkyl halides produces organometallic compounds:

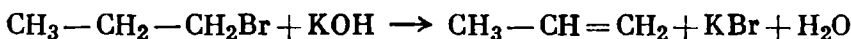


The action of magnesium upon the alkyl halides in the presence of absolute ethyl ether produces solutions containing mixed organo-magnesium compounds (Grignard reagent):



In the next chapter we shall consider the organometallic compounds in greater detail.

5. A caustic alkali (solution in alcohol) removes a hydrogen halide from alkyl halides, this giving rise to an olefine:



By the subsequent addition of a hydrogen halide to the olefine, we can obtain an alkyl halide of different structure.

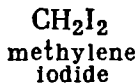
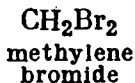
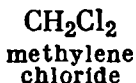
The iodides are the most reactive and the chlorides the least reactive among the alkyl halides.

Although the halogen atom in the alkyl halides is highly mobile the alkyl halides are not ionic compounds and in solution are either barely ionized or are ionized to an extremely insignificant degree. For this reason at an ordinary temperature they react very slowly with silver nitrate.

Ethyl chloride $\text{C}_2\text{H}_5\text{Cl}$ at a slight pressure condenses into a liquid, which boils at 13.1° . When a small amount of this liquid is poured on the skin, it evaporates rapidly, causing the sharp cooling of the adjacent flesh. It is by virtue of this property that ethyl chloride is used as a local anaesthetic in surgical operations.

Ethyl chloride is kept in glass break-seal ampules or hermetically sealed vials.

43. Dihalogen Derivatives of Saturated Hydrocarbons. The simplest dihalogen derivatives of saturated hydrocarbons are the derivatives of methane:

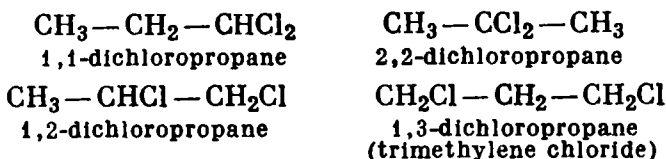


They can be regarded as halogen compounds of the divalent radical $\text{CH}_2\text{<}$, called *methylene*.

From ethane C_2H_6 we can obtain two isomeric dihalogen derivatives: ethylene dichloride $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ (1,2-dichloroethane) and ethylidene chloride $\text{CH}_3-\text{CHCl}_2$ (1,1-dichloroethane). In the ethylene dichloride molecule the chlorine atoms are attached to different carbon atoms, while in the ethylidene chloride molecule they are attached to the same carbon atom.

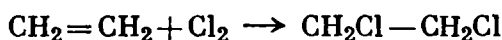
The divalent radical $-\text{CH}_2-\text{CH}_2-$ is called *ethylene*, and the divalent radical CH_3-CH is called *ethylidene*.

Propane $\text{CH}_3-\text{CH}_2-\text{CH}_3$ has four isomeric dihalogen derivatives:



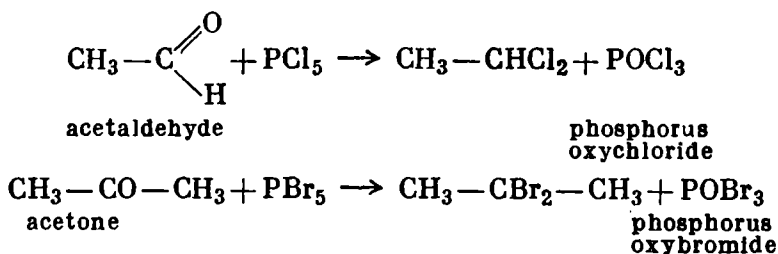
The dihalogen derivatives of saturated hydrocarbons may be prepared:

1. By the addition of a halogen to olefines:



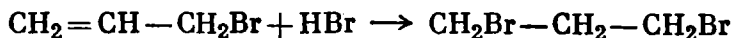
Substances with halogen atoms attached to neighbouring carbon atoms are prepared in this way.

2. By the action of phosphorus pentachloride or pentabromide on aldehydes or ketones:



The resulting substances have two halogen atoms attached to the same carbon atom.

Dihalogen derivatives with the halogen atoms attached to non-neighbouring carbon atoms can be prepared by the interaction of unsaturated halogen derivatives with HBr in the presence of peroxides (p. 170):



The hydrogen bromide is in this case added contrary to Markovnikov's rule.

The dihalogen derivatives of saturated hydrocarbons are heavy oils or solids that are insoluble in water.

Methylene iodide CH_2I_2 is a very heavy liquid; its density is 3.333 at 15° . It boils at 180° . It is used in mineralogy to separate minerals according to density. Methylene iodide was first prepared by Butlerov in 1858.

Ethylene dichloride, or 1,2-dichloroethane, $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ is a liquid (density 1.25 at 20°) boiling at 84° .

It is prepared by the addition of chlorine to ethylene; it is used as a solvent, as a fumigant against barn pests, and is an intermediate product in the manufacture of glycol $\text{CH}_2(\text{OH})-\text{CH}_2(\text{OH})$.

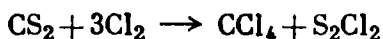
Ethylidene chloride $\text{CH}_3-\text{CHCl}_2$ is a liquid (density 1.189 at 0°) boiling at 58° .

44. Polyhalogen Derivatives of Saturated Hydrocarbons. The most important of the halogen derivatives with several halogen atoms in the molecule are the halogen derivatives of methane: chloroform CHCl_3 , iodoform CHI_3 , and carbon tetrachloride CCl_4 .

Chloroform CHCl_3 is prepared from alcohol or acetone by the action of an alkaline solution of chlorine or bleaching powder (p. 196). It is a liquid with a characteristic sickly sweetish smell; it boils at 61.2° . Its density is 1.498 at 15° . When exposed to the action of light and air, it is oxidized, yielding Cl_2 , HCl , CO_2 , and phosgene COCl_2 . Inhalation of chloroform vapour causes loss of consciousness (anaesthesia). Hence its use in surgical operations.

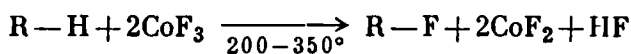
Iodoform CHI_3 may be prepared, like chloroform, from alcohol or acetone by the action of iodine and an alkali. Iodoform crystals are of a lemon yellow colour with a characteristic odour of saffron. They sublime very easily, melting at 119° . Iodoform is used as a disinfectant for wounds.

Carbon tetrachloride CCl_4 is prepared by the action of chlorine upon carbon disulphide:



Carbon tetrachloride is a liquid boiling at 76.5° ; its density is 1.58 at 21° . Its vapour is absolutely nonflammable. Carbon tetrachloride is used as a solvent for resins, fats, rubber, and other substances, as well as a fire-extinguishing agent (in special fire extinguishers).

45. Fluoroderivatives of Saturated Hydrocarbons. Free fluorine reacts with hydrocarbons very violently, the hydrocarbons being completely charred. Fluorination is conducted by passing the vapour of the saturated hydrocarbon, mixed with nitrogen, through a layer of cobaltic fluoride, at a high temperature:

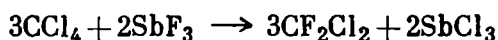


By gradually replacing all the hydrogen atoms in saturated hydrocarbons with fluorine, we obtain carbon perfluorides. As a hydrogen substitute, fluorine occupies a position all its own. The presence of at least two fluorine atoms attached to a single carbon atom in the molecule makes a substance chemically stable. All the carbon perfluorides are stable compounds; they do not decompose even upon

heating to 400-500°. The perfluorides prepared so far include *tetrafluoromethane* CF_4 , which is a gas that condenses to a heavy liquid boiling at -128° , and *hexafluoroethane* C_2F_6 , likewise a gas (b.p. -78.2°). Many carbon perfluorides are known, up to the hexadecane compound $\text{C}_{16}\text{F}_{34}$, colourless plates melting at 115° .

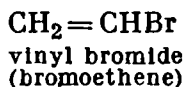
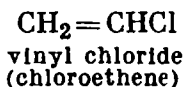
The fluorine derivatives with the most extensive applications are the low-boiling compounds whose molecules contain both fluorine and chlorine, such as CF_2Cl_2 , dichlorodifluoromethane. In industry these substances are known as *freons*; they are used in refrigeration.

Dichlorodifluoromethane CF_2Cl_2 is under ordinary conditions a colourless and odourless gas, which condenses and boils at -30° . It is prepared from carbon tetrachloride and antimony trifluoride in the presence of bromine or antimony pentachloride to initiate the reaction:



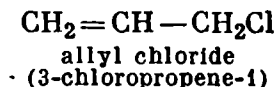
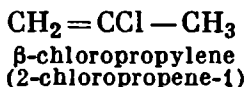
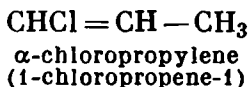
Dichlorodifluoromethane is a stable compound. Its vapours are not toxic. In this compound both chlorine and fluorine are unreactive.

46. Halogen Derivatives of Unsaturated Hydrocarbons. The simplest halogen derivatives of the olefines are the halogen derivatives of ethylene:



They may be regarded as halogen compounds of the monovalent radical vinyl $\text{CH}_2=\text{CH}-$.

Three isomers are possible for the monohalogen derivative of propylene:



According to the reactivity of the halogen atoms, the monohalogen derivatives of the ethylene hydrocarbons may be divided into two groups:

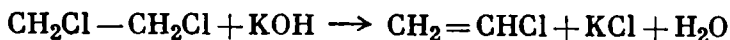
- 1) compounds in which the halogen atom is attached to a carbon atom linked to another carbon atom by a double bond;
- 2) compounds in which the halogen atom is attached to some other carbon atom.

The compounds of the first group include vinyl chloride, and also α - and β -chloropropylene; the compounds of the second group are exemplified by allyl chloride.

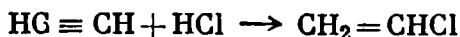
The compounds of the first type may be prepared:

1. By the removal of one molecule of hydrogen halide from dihalogen derivatives in whose molecules the halogen atoms are attached

to the same carbon atom or to two neighbouring carbon atoms:



2. By the addition of one molecule of hydrogen halide to an acetylene hydrocarbon:



Compounds of this type differ markedly from the alkyl halides in chemical character. In the alkyl halides the halogen atom is easily replaceable by a hydroxyl or other group. But compounds in which the halogen is attached to a doubly bound carbon atom are practically incapable of such reactions: the halogen atom in them is immobile. Halogen compounds of the allyl chloride type, on the contrary, enter into exchange reactions more readily than the alkyl halides do.

Vinyl chloride $\text{CH}_2=\text{CHCl}$ is a gas (b.p. -13°). It polymerizes quite readily, forming high-molecular compounds, and is used to manufacture plastics.

Allyl chloride, bromide, and iodide $\text{CH}_2=\text{CH}-\text{CH}_2\text{X}$ ($\text{X}=\text{Cl}$, Br , I) are liquids boiling at 45° , 71° , and 103° , respectively; they have a mustard-like odour. Allyl chloride and allyl bromide are prepared by the action of phosphorus pentahalides or hydrogen halides on allyl alcohol $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$.

Tetrafluoroethylene $\text{CF}_2=\text{CF}_2$ is a colourless and odourless gas (b.p. -76.3°). It is prepared by the pyrolysis of difluorodichloromethane:



47. High-Molecular Compounds. Plastics. Unsaturated hydrocarbons and their halogen derivatives undergo polymerization (pp. 81 and 112). The polymerization products are high-molecular compounds with molecular weights ranging from a few hundred to a million and higher. They have found extensive application in the production of various synthetic materials: plastics, synthetic rubber, synthetic fibre, glue, ion-exchange resins, etc.

Plastics are those high-molecular compounds that, under the influence of high temperature and pressure, can be converted to the plastic state and moulded into any shape. Unlike synthetic rubber, plastics exhibit little or no elasticity at an ordinary temperature. Although their production began a mere half-century ago, plastics have acquired enormous industrial and household uses. They are being substituted successfully for metals and wood, glass and precious stones, china and cut-glass. Besides this, they have become indispensable materials in machine-building, the automobile industry, the aircraft industry, shipbuilding, electrical engineering, the chemical industry, and many other branches of the national economy.

Plastics have often been found to combine several valuable properties. Steel is an example of a strong material; wood and aluminium are examples of light and hard materials; glass is an example of a transparent material. However, steel is vulnerable chemically—it rusts; moreover, it does not lend itself readily to mechanical treatment. Similarly, wood rots; furthermore, it is not transparent and is a poor electric insulator. Finally, glass is fragile and, likewise, does not lend itself to mechanical treatment readily in the cold state. Plastics, on the other hand, do not have these shortcomings. Most plastics are light, are good insulators, are very strong, and yield readily to mechanical treatment. Many plastics are transparent, do not rot, resist the action of strong acids and alkalis, etc.

The basic material of a plastic is the *high-molecular substance (resin)*. Resins may be either natural (rosin, pitch, asphalt) or synthetic (polymerization or polycondensation products of organic compounds). The synthetic resins are at present the more important.

Polymerization and polycondensation differ from one another.

In *polymerization* identical molecules combine without the elimination of simple molecules, and the molecular weight of the resulting polymer is equal to the sum of the molecular weights of the reacting molecules. If the polymer is formed by the combination of different substances, this is called composite polymerization or copolymerization.

In *polycondensation* simple molecules combine to form a polymer with the elimination of simple substances, such as H_2O , HCl , NH_3 , and, consequently, the molecular weight of the polymer is not equal to the sum of the weights of the initial molecules.

Synthetic resins are usually prepared in the presence of substances accelerating the process of polymerization.

For instance, polyvinyl chloride ($-\text{CH}_2-\text{CHCl}-$)_n—the polymer of vinyl chloride—is prepared by polymerizing vinyl chloride $\text{CH}_2=\text{CHCl}$ in aqueous emulsions in the presence of peroxide substances. (For the polymerization of ethylene and isobutylene see pp. 87-88.)

High-molecular compounds are either viscous liquids or solids, which often become soft upon heating. It is customary to classify plastics and distinguish them according to the chemical character of the resin, e.g., polyvinyl chloride plastics, phenol formaldehyde plastics, and melamineformaldehyde plastics.

Some plastics, such as polythene and the polyamides, consist entirely of polymer; in others the content of high-molecular compounds does not exceed 20-60%, while the rest is filler (wood flour, glass wool, asbestos, etc.). Fillers serve to change the properties of plastics in a desirable direction—to make them strong, hard, flame resistant, etc. Fillers are used extensively in making plastics from phenol-formaldehyde, urea-formaldehyde, epoxy, and certain other resins.

The conversion of some polymers, such as polyvinyl chloride, into plastics requires the use of what are known as *plasticizers*.

Plasticizers are substances imparting plasticity to a polymer, i.e., facilitating the conversion of solid and brittle resins to a dough-like condition convenient for moulding them into the desired shape. By adding more plasticizers, it is possible to obtain flexible and quite elastic materials resembling rubber.

Polyvinyl chloride resin is either a solid mass or a fine white powder. By mixing it with plasticizers (ordinarily esters of phthalic acid or phosphoric acid) and either compressing it or passing it through calender rolls, it can be turned into a plastic suitable for making various articles like footwear, handbags, mackintoshes, and oil cloths.

In many cases a composition will include what are known as *stabilizers*, ingredients protecting the high-molecular compound from decomposition throughout the processing and from the action of light and heat during the service life of the composition. Dyes too may be added to impart the necessary colour to the product.

Synthetic Materials Based on Vinyl Polymers

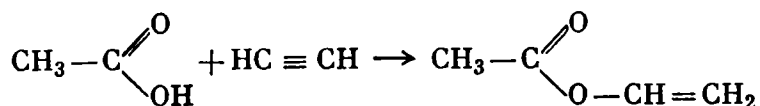
Vinyl chloride $\text{CH}_2=\text{CHCl}$ under the action of light or upon heating forms a polymer, which is a white amorphous powder.

Cheap, accessible, and nonflammable, plastics from polyvinyl chloride find many industrial and household applications.

Plasticized polyvinyl chloride is used in large quantities for the insulation of communication cables and wires; in this role it simultaneously replaces rubber, lead, and cotton yarn. Other of its applications are in the production of imitation leather, linoleum, mackintoshes, cloaks, handbags, and various household articles. Polyvinyl chloride processing without plasticizers yields *unplasticized polyvinyl chloride*, a rigid material, which lends itself readily to welding and machining. It is used to make fume ducting, pumps, and various apparatus parts.

Chlorination of polyvinyl chloride produces *pervinyl chloride resin*. In the form of lacquers and glues it is used to coat apparatus; a fibre is also made from it.

Vinyl Acetate $\text{CH}_2=\text{CHOCOCH}_3$. Vinyl acetate is prepared by a gaseous-phase reaction between acetylene and acetic acid:



Vinyl acetate is polymerized to *polyvinyl acetate*, which is used extensively to make water-base paints. Such paints may be applied without solvents. Other applications of polyvinyl acetate are as

a textile finish that makes fabrics crease-resistant and as glue compositions for paper, leather, wood, metals, etc.

Copolymers of vinyl chloride and vinyl acetate serve as a basis for producing high-grade lacquer-forming resins and resins for long-playing gramophone records.

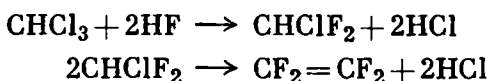
Copolymers of vinyl chloride and vinylidene chloride $\text{CH}_2=\text{CCl}_2$ are used industrially to make coating resins for long-playing records. These copolymers are also used to make pipes, inserts, and a synthetic fibre that is not very suitable for garments, but serves to manufacture upholstery, decorative and certain other fabrics.

Fluorine-containing polymers

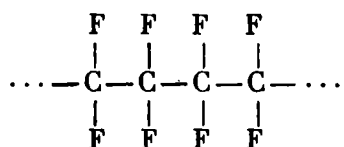
The introduction of not less than two fluorine atoms into the hydrocarbon molecule greatly increases the general stability of the compound. Thanks to this, fluorine-containing polymers show an unsurpassed thermal stability and resistance to chemical attack.

Hydrocarbons cannot be fluorinated directly because of the destruction of their molecules. Fluorocarbons and completely fluorinated substances consisting of fluorine and carbon are therefore from the corresponding chlorine derivatives.

Tetrafluoroethylene $\text{CF}_2=\text{CF}_2$. This is a colourless gas; the boiling point of the compound is -76° . Tetrafluoroethylene is prepared from chloroform:



The compound polymerizes readily at 60° and moderate pressure in the presence of peroxide compounds. The resulting polymer has a regular linear structure:



Plastics based on polytetrafluoroethylene, or PTFE, are known as Teflon plastics. They are distinguished by a high thermal stability in the range from -183° to 300° and by a high resistance to chemical attack. These plastics are unaffected by hot fuming nitric acid, by concentrated sulphuric acid, or by molten sodium hydroxide. Only molten metallic sodium destroys them gradually.

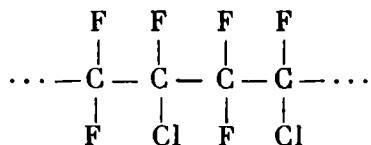
Teflon is an invaluable material in manufacturing critical instrument parts and apparatus units operating in highly corrosive

conditions, including insulating materials, inserts used in chemical engineering, and special films.

A disadvantage of Teflon is the need for special fabricating techniques, since it does not dissolve in any solvent, does not have a definite melting point, and has a low flowability even when softened.

Plastics Based on Polychlorotrifluoroethylene

Chlorotrifluoroethylene $\text{CF}_2=\text{CFCl}$ is a colourless gas, which condenses at -27° . It relatively easily polymerizes at room temperature into polychlorotrifluoroethylene:



Polychlorotrifluoroethylene is somewhat inferior to PTFE in thermal stability and resistance to chemical attack, but is more easily fabricated.

The copolymer of polychlorotrifluoroethylene and vinylidene fluoride $\text{CH}_2=\text{CF}_2$, which contains more than 50% fluorine by weight, possesses good elastic properties and belongs to the group of fluororubbers. It is used wherever rubber goods have to stand up to high temperatures or aggressive chemicals.

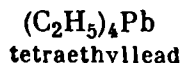
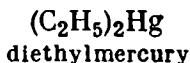
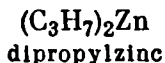
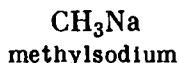
Organoelement Compounds

48. Organoelement Compounds and Their Importance. When we consider the composition of organic substances, we are quick to notice that, apart from the omnipresent carbon, they most frequently contain the following elements: hydrogen, oxygen, nitrogen, sulphur, and the halogens. These elements are often referred to as typical organogens. However, both natural and, especially, artificially prepared products number very many substances that also contain other elements (non-organogens): the metals Na, K, Al, Zn, Mg, Hg, Pb, and Sn, and also the non-metals P, Si, B, and As.

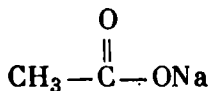
It goes without saying that such a division of the elements into organogens and non-organogens is highly relative, but then the customary division into metals and non-metals is just as relative (e.g., As, Te, and I).

The first of the organoelement compounds to be discovered (Frankland, 1849) were compounds containing a metal. Owing to their extraordinary reactivity, these compounds acquired great importance and were singled out as a special group, the so-called *organometallic compounds*. Further advances in organic chemistry extended the term to take in compounds containing non-metals, and it is now customary to refer to them as *organoelement compounds*.

Only those organic compounds containing some metal (or non-metal) in which the atom of that element is linked directly to a carbon atom are called organoelement compounds. Examples of such compounds are provided by

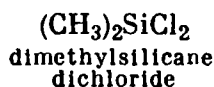
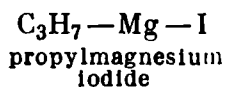
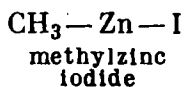


It would thus be wrong to regard as organoelement compounds the salts of carboxylic acids, alkoxyds, phosphoric acid esters, and other compounds in which the atoms of the metal, phosphorus or other non-organogen element are linked to the hydrocarbon radical not directly, but, say, through an oxygen atom:



As seen from the examples of organoelement compounds given above, the atoms of different elements combine with a different number of radicals.

Bivalent and polyvalent metals can form two types of organometallic compounds: simple and mixed. In the compounds of the first type the atom of the metal is linked only to the hydrocarbon radicals, while in the compounds of the second type there is an inorganic radical, besides the organic one. Examples of simple organometallic compounds have been given above. The following are examples of mixed organometallic compounds:



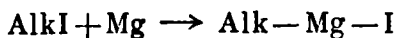
The simple organometallic compounds are mostly liquids, which may be distilled without decomposition. Organosodium and organomagnesium compounds decompose upon heating. As volatile substances, organometallic compounds have been used to determine the atomic weights and valencies of various metals (aluminium, tin, and lead).

The bond between the metal atom and the carbon is not strong, and the metal readily makes room for other atoms or radicals. The high reactivity of organometallic compounds makes it possible to use them for preparing a number of substances. The compounds of zinc and magnesium are especially important in organic synthesis.

Organometallic compounds have played a big role in the development of organic chemistry, especially its synthetic methods. In the latter half of the past century A. Butlerov, A. Zaitsev, Y. Wagner, F. Beilstein, S. Reformatsky, and their disciples evolved methods of preparing ketones, tertiary and secondary alcohols, and certain organometallic compounds by means of organozinc compounds.

Mixed organomagnesium compounds, first studied by Grignard*, are of quite exceptional importance in organic syntheses.

* François August Victor Grignard, famous French organic chemist (1871-1935). His best known work was in the synthesis and application of mixed organomagnesium compounds. He demonstrated that metallic magnesium reacts with alkyl iodides dissolved in thoroughly dehydrated ether, producing an ethereal solution of mixed organomagnesium compounds:



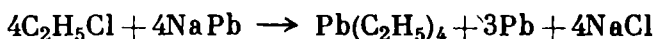
Grignard proceeded from the Zaitsev reaction—the interaction of alkyl iodides with zinc—and substituted magnesium for zinc, using anhydrous ether as a solvent. This considerably extended the applications of organometallic compounds, since magnesium is a more active metal and can react not only with alkyl and aryl iodides (as zinc does), but also with bromides and chlorides (p. 119). For his discovery of the organomagnesium compounds Grignard was in 1912 awarded the Nobel Prize.

They can be instrumental in preparing substances belonging to the most diverse classes of organic compounds (hydrocarbons, alcohols, ethers, ketones, aldehydes, carboxylic acids, esters, and nitriles), as well as other organometallic compounds.

Tetraethyllead $(C_2H_5)_4Pb$ holds a very special position among the organometallic compounds. The use of this substance as a highly effective anti-knock agent* has led to large-scale production plants being established in a number of countries for its manufacture.

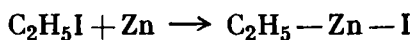
Tetraethyllead $(C_2H_5)_4Pb$ is a heavy colourless liquid (relative density about 1.65) with an unpleasant odour.

It is prepared by the action of ethyl chloride on an alloy of lead and sodium:

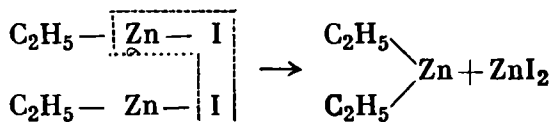


Tetraethyllead vapours are highly poisonous.

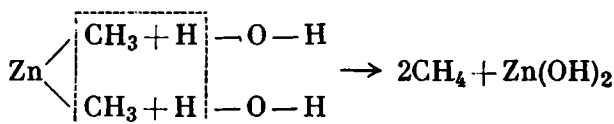
49. Organozinc Compounds. Organozinc compounds may be prepared by heating alkyl iodides with zinc. The reaction consists of two phases. First, a mixed organometallic compound is formed, such as crystalline ethylzinc iodide



which is then at a high temperature converted to liquid diethylzinc:



When exposed to air, organozinc compounds ignite spontaneously and burn with a blue flame. Water decomposes them into hydrocarbons and zinc hydroxide:



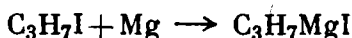
Owing to the readiness with which organozinc compounds ignite spontaneously, all work with them is conducted in an atmosphere of dry carbon dioxide, hydrogen, or nitrogen.

50. Organomagnesium Compounds. Organomagnesium compounds are prepared by adding an alkyl halide to metallic magnesium

* Anti-knock agents are substances added to petrol in order to lessen its tendency to detonate in the cylinders of internal combustion engines (p. 82).

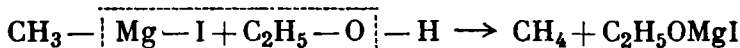
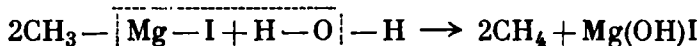
turnings under a layer of thoroughly dehydrated ether*. The reaction proceeds so vigorously that the ether starts boiling.

It results in the formation of a mixed organometallic compound $R-Mg-X$ (where R is a radical, and X , a halogen), e.g.:



The organometallic compounds prepared in this way are bound chemically with the ether. However, they react in the same way as do organomagnesium compounds from which the ether has been removed. It is therefore customary not to isolate them from the solution, but to use them in this form for subsequent syntheses. Individual organomagnesium compounds, i.e., those from which the ether has been removed, may be prepared, as demonstrated by V. Chelintsev, by adding magnesium turnings and a few drops of ether or dimethylaniline (which in this case act merely as catalysts) to a benzene solution of an alkyl halide.

Mixed organomagnesium compounds do not ignite upon exposure to the air. Water, alcohols, and other substances containing the hydroxyl group (as well as primary and secondary amines) easily decompose these compounds with the formation of hydrocarbons:

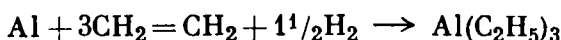


This forms the basis of the method proposed by L. Chugayev in 1920 and elaborated by F. Tserevitinov for the quantitative estimation of hydroxyl groups in organic compounds: a weighed quantity of the substance that is being investigated is treated with methylmagnesium iodide, and the volume of the methane evolved is measured.

51. Organoaluminium Compounds. These compounds are usually prepared by reactions between alkyl iodides and aluminium:



Industrially trialkylaluminium is produced from the corresponding olefine, hydrogen, and finely divided aluminium at 100-120° under pressure:



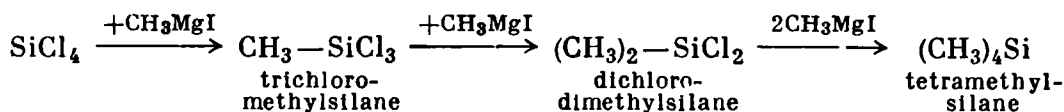
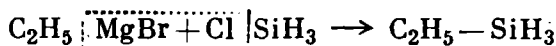
* Without ether, metallic magnesium reacts with alkyl halides with difficulty. It is customary to look upon the ether as a catalyst of this reaction.

Trimethylaluminium $\text{Al}(\text{CH}_3)_3$ is a liquid, which boils at 130° and ignites upon exposure to air. *Triethylaluminium* $\text{Al}(\text{C}_2\text{H}_5)_3$ boils at 194° . Primary, secondary, and tertiary (complete) derivatives are known for aluminium.

Organoaluminium compounds have industrial uses, since a number of important industrial syntheses can be carried out with their aid. For example, polythene of unbranched structure (p. 87) can be produced in the presence of triethylaluminium.

52. Organosilicon Compounds. Silicon, like carbon, is in Group IV of the Periodic Table and is the analogue of carbon in its simplest compounds. In their chemical properties, however, the compounds of carbon and of silicon differ very markedly. This applies, first and foremost, to the ability to form chains: whereas carbon is characterized by compounds containing diverse chains of C—C atoms, silicon is incapable of forming chains consisting of more than six Si atoms. The silicon hydrides, or *silanes*, are highly unstable compounds, which ignite spontaneously upon exposure to air. The first few members of the silane series are either gases or low-boiling liquids: monosilane SiH_4 (b.p. -112°), disilane Si_2H_6 (b.p. -44°), and trisilane Si_3H_8 (b.p. 53°).

Equally unstable and highly reactive are the chlorine derivatives of the silanes: chlorosilane SiH_3Cl , trichlorosilane (silicochloroform) SiHCl_3 , and silicon tetrachloride SiCl_4 . All these substances are vigorously hydrolyzed by water. With organozinc and organomagnesium compounds they form organosilicon compounds (alkylsilanes):

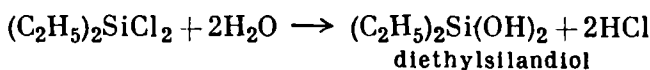


In practice an alkyl halide and magnesium are used instead of mixed organomagnesium compounds:

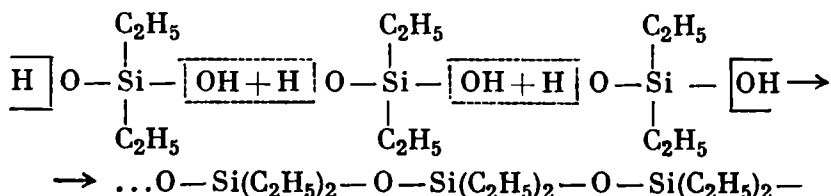


The most stable of the alkylsilanes are those that have no hydrogen atoms attached to the silicon: the tetraalkylsilanes.

The alkylchlorosilanes have a practical application: hydrolysis causes them to yield *silanols* (or *silicols*):



The dialkylsilandiols are highly unstable: they readily condense, with the elimination of water, producing *siloxanes*, or so-called *silicones*:

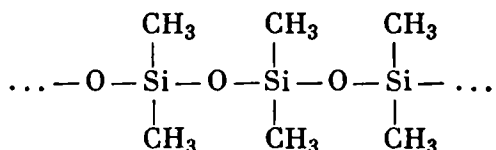


This ability to form *siloxane chains* is characteristic of silicon.

The organosilicon polymers can be liquid or solid, brittle or highly elastic, resembling rubber. Their most important distinctive feature is their higher heat resistance than that of organic polymers proper.

The ability to withstand both very low (-100°) and very high temperatures (300° and higher) has made the organosilicon polymers very important materials in modern industry, especially in the electrical industry to increase the reliability of electric motors in mines, transport, etc., and also in radio engineering and in the aircraft industry.

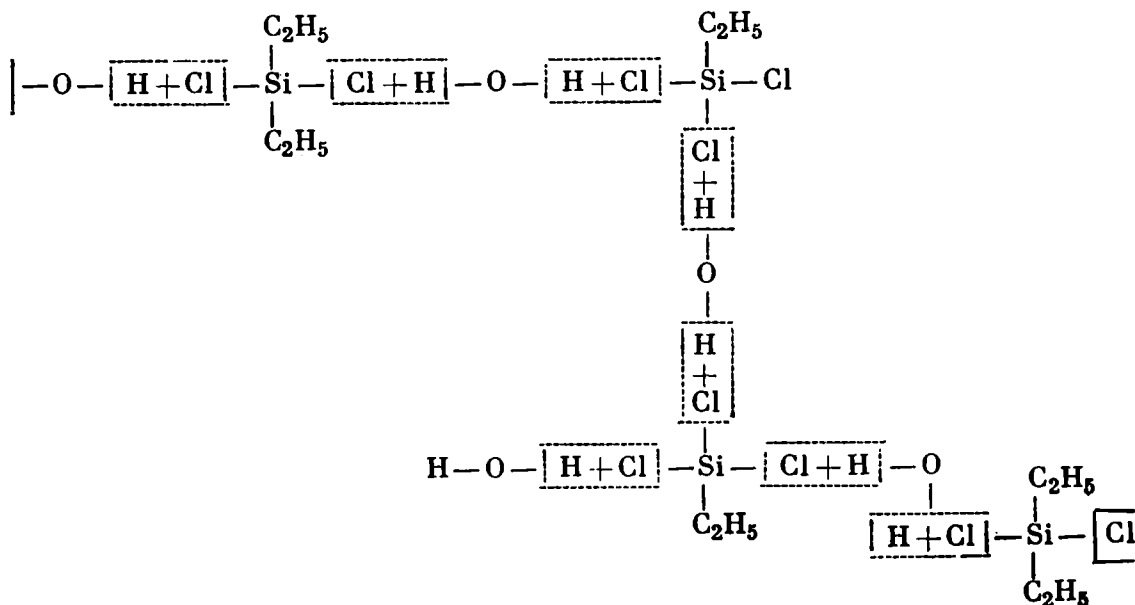
The hydrolysis of dichlorodimethylsilane yields an elastic organosilicon polymer known as *silicone rubber*. The siloxane chain in this case has the structure:



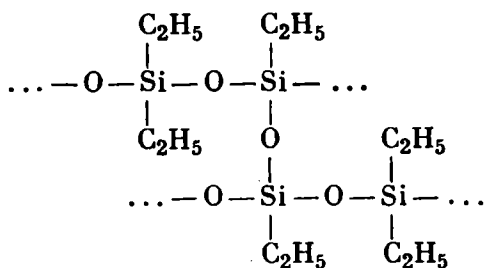
Silicone rubber is white and has a relatively low mechanical strength, but it is indispensable wherever a material is required to retain its elastic properties within a wide temperature range.

Organosilicon polymers also have other important industrial applications. Silicone lubricants have found many applications; they have a high heat resistance and a practically constant viscosity in a broad temperature range. Such lubricants are also used in laboratory work: they are very stable and are not oxidized even by such a strong oxidizing agent as ozone.

The polymer molecules are symmetric and therefore lack polarity; for this reason such substances are insulators. The hydrocarbon radicals impart water-repellent properties to them, which are a factor of prime importance in determining a number of their technical applications. Materials are now made, for example, which are waterproof, but not air-tight (cardboard, porcelain, bricks); this is achieved by treating them with the vapours of organosilicon compounds. The organosilicon compounds interact with water:



This causes waterproof silicone films to form in the pores of the material:



Plastics based on organosilicon compounds are used extensively in electrical engineering to make insulating materials resistant to heating.

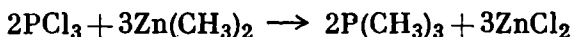
The work of K. Andrianov contributed greatly to building up the chemistry of polymeric organosilicon compounds.

53. Organophosphorus and Organoarsenic Compounds. Phosphorus and arsenic are, like nitrogen, in Group V of the Periodic Table. With hydrogen they form the compounds PH_3 and AsH_3 , similar to NH_3 . Phosphoretted hydrogen, like ammonia, can react with acids to give phosphonium salts, such as phosphonium iodide PH_4I . Phosphonium salts are less stable than ammonium salts and are easily hydrolyzed by water. Arseniuretted hydrogen, however, does not form salts with acids, because AsH_3 is but slightly basic.

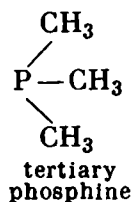
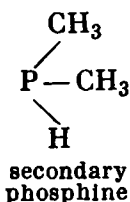
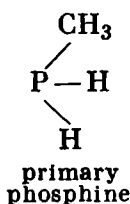
Just as there exist organic derivatives of ammonia (amines, see Chapter XIII), there can be organic derivatives of phosphoretted hydrogen (phosphine) and arseniuretted hydrogen (arsine).

Two types of organophosphorus compounds exist: *phosphines* and *phosphinic acids*.

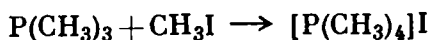
Phosphines are formed by the interaction of phosphorus trihalides with organometallic compounds:



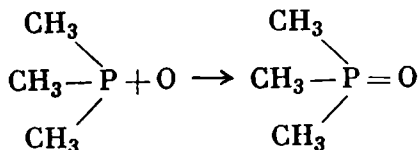
There are primary, secondary, and tertiary phosphines (by analogy to primary, secondary, and tertiary amines):



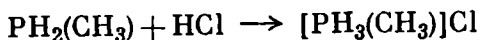
The introduction of alkyl groups into the phosphine molecule makes its basic character more pronounced, just as this is the case with ammonia derivatives. The tertiary phosphines, for instance, are capable of adding alkylhalides, forming quaternary phosphonium salts:



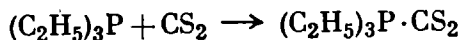
The phosphines are gaseous or liquid substances with an unpleasant odour; they are highly toxic and do not dissolve in water. When exposed to air, they oxidize readily and may even ignite spontaneously. Oxidation turns them into phosphine oxides:



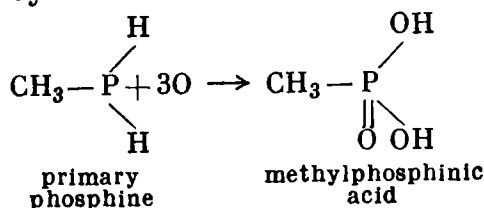
Aqueous solutions of phosphines are not alkaline (unlike amines), but with strong acids produce salts:

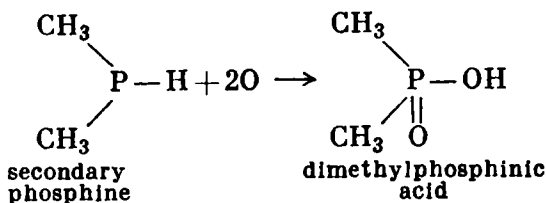


Tertiary phosphines are used for the qualitative detection of carbon disulphide by virtue of the fact that they form bright red addition products of low solubility:

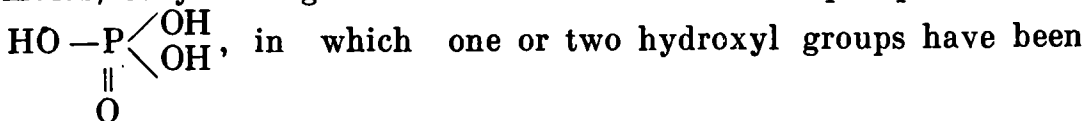


Phosphinic acids are formed when primary and secondary phosphines are oxidized by nitric acid:

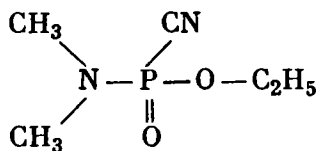




The alkylphosphinic acids, as evident from their structural formulas, may be regarded as derivatives of ortho-phosphoric acid



replaced by alkyls. The phosphinic acids are colourless crystalline substances, readily soluble in water. Noteworthy among their derivatives is *tabun*, the ethyl ester of *N*-dimethylaminocyanophosphinic acid:

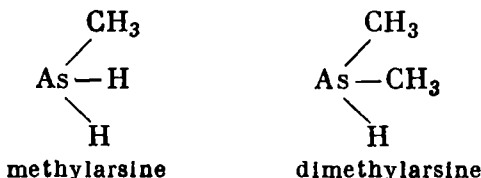


Tabun is a liquid with a low solubility in water at ordinary temperature; it has a faint fruit odour and is highly toxic. Its vapours have a toxic effect on the respiratory tract, penetrate through the skin and mucous membranes, cause headache and contraction of the pupils. High concentrations may be fatal.

Many phosphinic acid esters are used as insecticides. The acids and their derivatives have been studied extensively by A. Arbuzov and B. Arbuzov.

Arsenic produces compounds that are similar to phosphorus-containing organic compounds and are called *arsines*.

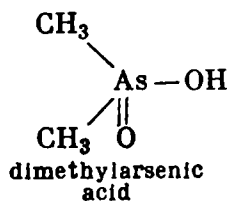
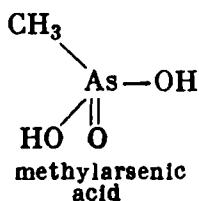
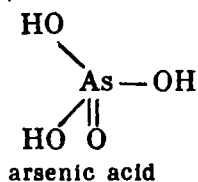
Arsines are substances of poor solubility in water; they have an unpleasant pungent odour and are highly toxic:



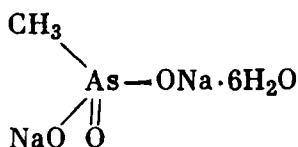
Arsines are oxidized very readily by the oxygen of the air. They are neutral substances incapable of forming salts.

Some of the arsines were used in the First World War as chemical warfare agents. The most poisonous of them is Lewisite (p. 93).

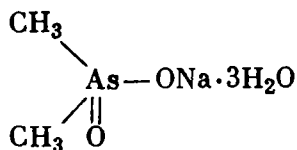
Arsinic acids may be regarded as derivatives of arsenic acid in which alkyls have been substituted for hydroxyls:



The arsinic acids are less toxic than the arsines. Some of the arsinic acids are used as drugs, e.g., *arrhenal*, the sodium salt of methylarsinic acid



and the sodium salt of dimethylarsinic (cacodyl) acid, sodium cacodylate



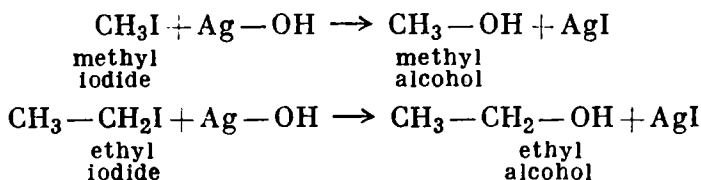
Alcohols and Their Derivatives

SATURATED MONOHYDROXY ALCOHOLS

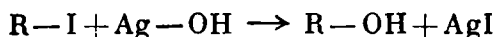
54. Structure of Alcohols. Representatives of the alcohol class have been encountered by us repeatedly in the preceding chapters. As stated above (p. 35), Wurtz, followed by Gerhardt, regarded the alcohols as derivatives of the water type in which one hydrogen atom has been replaced by a hydrocarbon radical:



This structure of the alcohols is confirmed by the interaction of alkyl halides with moist silver oxide, whose dissolved part reacts as a hydroxide:



In the general form this may be written as follows:



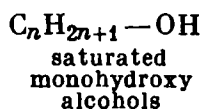
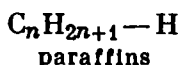
Even at low temperatures the halogen atom in alkyl halides can be replaced by a hydroxyl, with the formation of an alcohol and practically insoluble silver iodide; thanks to the latter fact, the reaction of alcohol formation proceeds to the end (is irreversible).

An alcohol may thus be regarded as a hydrocarbon in which one or more hydrogen atoms have been replaced by one or more hydroxyl groups. It should be borne in mind that the hydroxyl group hydrogen, linked to an oxygen atom, differs markedly in character from the hydrogen atoms linked to carbon atoms.

According to the number of hydroxyls they contain, alcohols may be monohydroxy, dihydroxy, trihydroxy, etc.

55. Alcohol Homology and Isomerism. Like the saturated hydrocarbons, the monohydroxy alcohols form a consecutive series of

homologues:



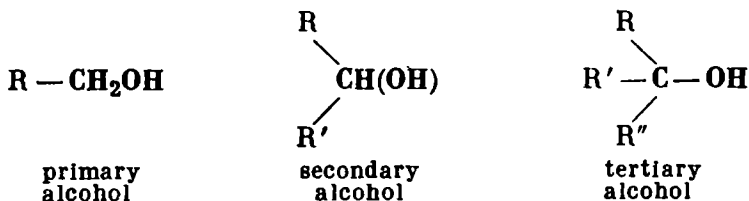
Just as in other homologous series, each member of the alcohol series differs from the member before and after it by the homologous increment CH_2 .

It will be seen at once that from the lower members of the series to the higher there is a drastic decline in the oxygen content and an increase in the carbon content:

	%C	%H	%O
CH_3-OH	37.48	12.58	49.93
$\text{C}_2\text{H}_5-\text{OH}$	52.14	13.13	34.73
$\text{C}_3\text{H}_7-\text{OH}$	59.96	13.42	26.62
$\text{C}_4\text{H}_9-\text{OH}$	64.81	13.60	21.59
$\text{C}_5\text{H}_{11}-\text{OH}$	68.13	13.72	18.15

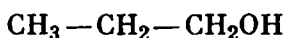
This accounts for the fact that methyl alcohol and ethyl alcohol burn with a colourless flame, while the higher alcohols burn with a smoking flame.

According to the type of carbon atom to which the hydroxyl is attached, we distinguish primary, secondary, and tertiary alcohols. The primary alcohol molecules contain the monovalent group $-\text{CH}_2\text{OH}$ linked to a single radical (the hydroxyl-bearing carbon atom is primary). The secondary alcohols contain the divalent group $>\text{CH}(\text{OH})$ connected with two radicals (the hydroxyl-bearing carbon atom is secondary). The tertiary alcohols contain the trivalent group $\text{>C}-\text{OH}$ linked to three radicals (the hydroxyl-bearing carbon atom is tertiary). If we denote the radical as R, we can write the general formulas of these alcohols as follows:



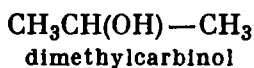
In number and character of isomers, the $\text{C}_n\text{H}_{2n+1}-\text{OH}$ alcohols are quite similar to the $\text{C}_n\text{H}_{2n+1}\text{Cl}$ alkyl halides. The number of possible isomers for the first few members of the alcohol series can be determined as follows. Let us take the simplest alcohol: methyl alcohol, or carbinol, $\text{H}_3\text{C}-\text{OH}$. If any one of the three hydrogen

atoms attached to the carbon is replaced by a methyl group, we obtain one and the same alcohol, $\text{CH}_3\text{—CH}_2\text{—OH}$, methylcarbinol, or ethyl alcohol. The next homologue $\text{C}_3\text{H}_7\text{—OH}$ has two isomers. The first isomer can be derived by substituting a methyl group for a hydrogen atom in the CH_3 group of ethyl alcohol:

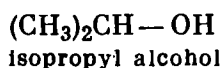


ethylcarbinol,
or *n*-propyl alcohol

The second isomer is obtained by replacing a hydrogen in the methylene group:



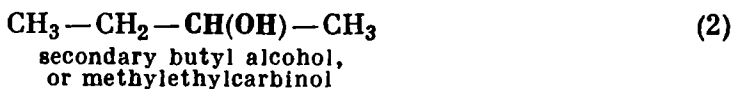
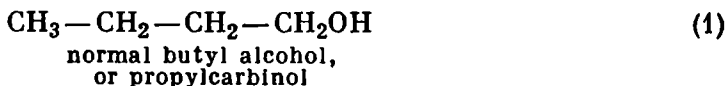
or
or



Both of these isomers have the same carbon skeleton corresponding to the hydrocarbon propane $\text{CH}_3\text{—CH}_2\text{—CH}_3$ and differ only in the position of the hydroxyl in the chain.

The next homologue $\text{C}_4\text{H}_9\text{—OH}$, however, has four isomers.

I. Two of them have carbon skeletons of normal structure:



II. The other two isomers have the carbon skeletons of isobutane (2-methylpropane):



isobutyl alcohol,
or isopropylcarbinol



CH_3
tertiary butyl alcohol,
or trimethylcarbinol

As we proceed towards the higher members of the series, the number of possible isomers* increases very rapidly:

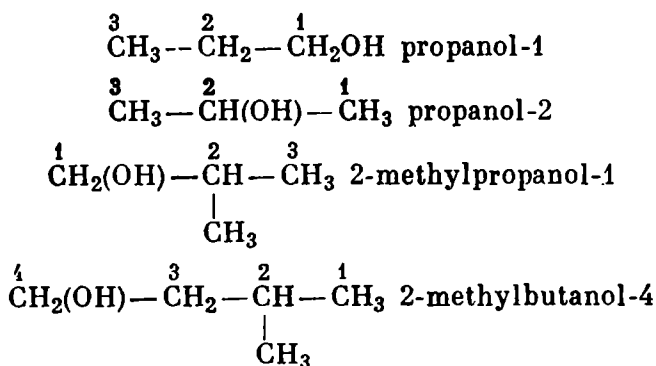
$\text{C}_1\text{—1}$	$\text{C}_5\text{—8}$
$\text{C}_2\text{—1}$	$\text{C}_6\text{—17}$
$\text{C}_3\text{—2}$	$\text{C}_7\text{—39}$
$\text{C}_4\text{—4}$	$\text{C}_{10}\text{—507}$

$\text{C}_{20}\text{—5,622,109}$

* These figures do not take into account stereoisomers (p. 152).

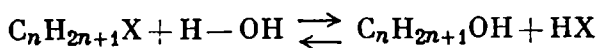
As may be seen from the above isomers (e.g., methylcarbinol, ethylcarbinol), in the simplest cases the names of the alcohols may be based on the old "carbinol" nomenclature: an isomer is regarded as a derivative of *carbinol* $\text{CH}_3\text{—OH}$ obtained by the substitution of corresponding radicals for its hydrogen atoms. However, this system proves adequate only in naming the simplest alcohols.

In the Geneva nomenclature the names of the alcohols are derived in the same way as the names of the hydrocarbons and the halogen derivatives. The name of the alcohol is based on the name of the hydrocarbon, with the presence of the hydroxyl group denoted by the ending *ol*, followed by a figure designating the number of the hydroxyl-bearing carbon atom. The numbering is done in such an order as to give the hydroxyl the smallest possible figure. The first two members of the series (methanol CH_3OH and ethanol $\text{C}_2\text{H}_5\text{OH}$) obviously require no figures.



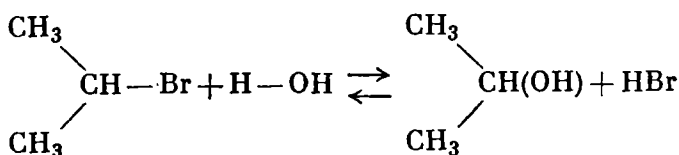
The last example shows that in the case of branched chains the carbon atoms are numbered from the end of the chain closer to the branch.

56. Preparation of Monohydroxy Alcohols. 1. One of the general methods of introducing the hydroxyl group into molecules of organic compounds is the hydrolysis of halogen derivatives of hydrocarbons in the presence of aqueous solutions* of alkalis:



where X is a halogen (Cl, Br, I).

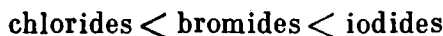
For example:



* It must be remembered that when halogen derivatives react with *alcoholic* solutions of alkalis, hydrogen halides are detached, with the formation of unsaturated bonds (p. 75).

The alkali accelerates the process and, by neutralizing the acid formed, makes it irreversible. It is easy to see that the carbon skeleton is unaffected by the reaction. Since the halogen in the halogen derivative is linked by a non-ionic bond and since halogen derivatives have a low solubility in water, the reaction requires prolonged heating.

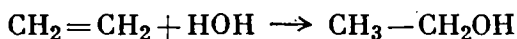
The tendency to undergo hydrolysis depends on the nature of the halogen. In detachment readiness the halogens form the following series:



This means that iodides can be hydrolyzed more easily than bromides or chlorides.

Halogen derivatives in which the halogen is linked to a tertiary carbon atom are hydrolyzed more easily than secondary, let alone primary, derivatives.

2. As pointed out above (p. 79), alcohols may be prepared by the action of water on ethylene hydrocarbons:

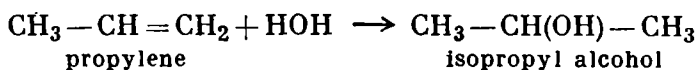


The reaction takes place when ethylene hydrocarbons are heated with water in the presence of catalysts: sulphuric acid, zinc chloride, etc. Ethylene yields a primary alcohol.

The reaction of ethyl alcohol formation from ethylene was thoroughly investigated by Butlerov. He prepared ethyl alcohol by hydrating ethylene in the presence of sulphuric acid. Nowadays alcohols are manufactured industrially by hydrating unsaturated hydrocarbons. Isopropyl alcohol, for instance, is prepared in large quantities from propylene. The need to replace food products as raw materials has led to the production of ethyl alcohol from ethylene: gaseous ethylene, obtained from petroleum cracking gases, is passed into sulphuric acid heated to 70° at a pressure of 10 atm.

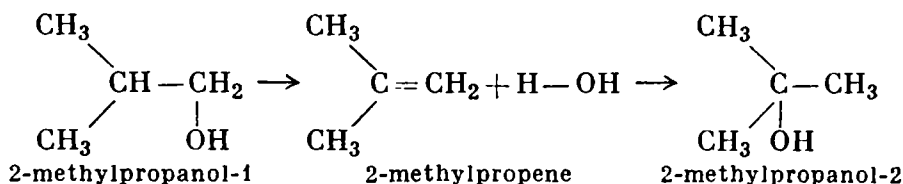
A more advanced method is based on the direct hydration of ethylene in the presence of solid catalysts.

The homologues of ethylene give secondary or tertiary alcohols. the addition of the water molecule obeying Markovnikov's rule. i.e., the hydrogen atom becomes attached to the most hydrogenated carbon atom (p. 77):



In this connection let us consider the process of preparing one alcohol from another. If we take, say, isobutyl (primary) alcohol, its dehydration will yield isobutylene. The hydration of isobutylene (i.e., addition of water to it) will give trimethylcarbinol, i.e., a ter-

tiary alcohol:



3. Alcohols can be prepared from aldehydes and ketones by reduction. Aldehydes produce primary alcohols; ketones, secondary. This is considered in greater detail on p. 180.

4. Amines of the general formula $\text{R}-\text{NH}_2$ (primary amines), when treated with nitrous acid, evolve nitrogen, turning into alcohols (p. 333). It should be borne in mind that this reaction proceeds in a complex manner and is often accompanied by isomerization.

5. The synthesis of alcohols by means of organozinc and organomagnesium compounds is highly important, particularly in laboratory work. This method makes it possible to prepare alcohols with a more complex carbon skeleton than that of the initial substances, which are in most cases aldehydes and ketones (p. 181), acid chlorides and esters.

6. Large amounts of ethyl alcohol are made industrially from vegetable materials containing starch: potatoes, rice, cereals, etc. Lately, however, various methods have been evolved for preparing alcohol from materials other than food. Ethyl alcohol, for instance, is prepared by the fermentation of a mixture of carbohydrates (glucose) obtained by the acid hydrolysis of the cellulose contained in sawdust and other waste materials of the timber industry. This is known as "*hydrolysis*" alcohol (it also contains a certain amount of methyl alcohol) and is used to manufacture synthetic rubber. Methods have been proposed for making alcohols by fermenting the hydrolysis products of young peat and of sulphite liquor (waste materials of the paper and pulp industry).

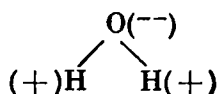
Large quantities of alcohol are manufactured, as said above (p. 130), by hydrating ethylene.

57. Physical Properties. A comparison of certain physical properties of several compounds within a homologous series reveals definite regularities. The boiling points of compounds of normal structure provide a particularly striking instance of this. With a growth of the number of CH_2 groups in saturated hydrocarbons, chlorine, bromine, and iodine derivatives, and primary alcohols, their boiling points rise steadily. A comparison of the properties of halogen derivatives shows at once that the substitution of Cl, Br, or I for a hydrogen atom in one and the same hydrocarbon molecule increases the molecular weight and sharply elevates the boiling point. But if a Cl atom (equivalent weight 35.5) is replaced by the lighter

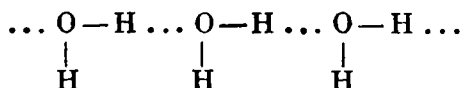
OH group (equivalent weight 17), the boiling point, far from declining, rises considerably, e.g.:

	Molecular weight	B.p., °C.
$\text{C}_2\text{H}_5\text{Cl}$	64.5	13
$\text{C}_2\text{H}_5\text{Br}$	108.91	38.4
$\text{C}_2\text{H}_5\text{I}$	155.91	72.3
$\text{C}_2\text{H}_5\text{OH}$	46.0	78.4

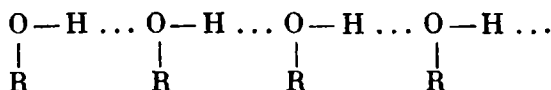
What is the reason for this? It will be remembered that the hydrogen halides (gases) boil at a much lower temperature than water does. A comparison of water and alcohol at once reveals their similarity. Both, for example, contain the hydroxyl group. The bond between the oxygen and the hydrogen in the alcohol molecule, as in the water molecule, is partly ionic. It will be recalled (p. 65) that in the water molecule the bonds between the hydrogen and the oxygen atoms form a certain angle, with the oxygen at the apex. Owing to this, the distribution of electric charges in the water molecule is asymmetric, and this gives rise to a rather considerable dipole moment ($\mu = 1.85$); between the oxygen and the hydrogen there arises a partly ionic bond, with the partial negative and positive charges appearing on the oxygen and the hydrogen being about equal to a third of an electron charge:



Because of the polar character of the water molecules, they are mutually attracted; for this reason water is an associated compound (H_2O)_x:



The dipole moment of ethyl alcohol ($\mu = 1.7$) is close to that of water. The alcohol molecules likewise interact to form associations:



The abnormally high boiling points of methyl alcohol and water, compared with the boiling points of methyl iodide or hydrogen iodide, are due precisely to this association.

In the series of alcohols of normal structure, as in other homologous series, the boiling points rise systematically from lower to higher

homologues. It should also be noted that among the isomers the tertiary alcohols have the lowest boiling points, while the primary unbranched alcohols have the highest.

The similarity of alcohols and water is also reflected in their solubility. Methyl, ethyl, and propyl alcohols are miscible with water in all proportions. Water molecules, like alcohol molecules, have high dipole moments, and for this reason there may be interaction between them too. This accounts for the high solubility of the above-mentioned alcohols in water. In addition to this, alcohol can form hydrates with water, which is evidenced by the rise in temperature when alcohol is mixed with water and by the fact that the volume of the mixture is less than the sum of the volumes of the alcohol and the water.

The butyl and amyl alcohols have a limited solubility in water, while the higher alcohols are insoluble in water. The solubility of tertiary alcohols is higher than the solubility of primary and secondary alcohols with the same number of carbon atoms in the molecule.

TABLE 4. Physical Properties of Butyl Alcohols

Alcohol	Formula	M.p., °C	B.p., °C at 760 mm	Solubility in 100 g of water at 20° in g
Normal butyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	-89.6	117.9	8.3
Isobutyl	$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	-108	108.1	9.5
Secondary butyl	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	-114.7	99.5	13
Tertiary butyl	$(\text{CH}_3)_3\text{C}(\text{OH})$	25.5	82.8	miscible in all proportions

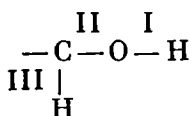
The relative densities of the alcohols are less than 1, i.e., they are all lighter than water. The lower alcohols have a faint characteristic odour; the odour of the intermediate members of the series is strong and at times unpleasant.

58. Chemical Properties. The alcohols have neither acid nor basic properties. Neither they nor their aqueous solutions conduct electricity at all appreciably. The bonds between their atoms are homoeopolar (p. 62 fol.):



Thanks to their availability and ability to enter into numerous chemical reactions, alcohols play an enormous part in all kinds of syntheses.

The various types of chemical transformations of the alcohols will be considered below in the following order of the participation of their constituent atoms in these transformations:



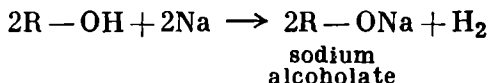
I. Reactions involving only the hydrogen atom of the hydroxyl group.

II. Reactions due to the properties of the hydroxyl itself.

III. Oxidation reactions involving both the hydroxyl and hydrogen atoms of the radical, while in some cases they even involve carbon atoms (tertiary alcohols).

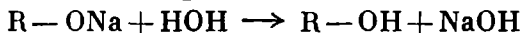
I. Reactions Involving the Hydroxyl Group Hydrogen. The hydrogen of the hydroxyl is highly mobile and easily replaced.

1. *Substitution of a metal for the hydroxyl hydrogen.* The substances resulting from this substitution are called *alcoholates*, or *alkoxyds*:



The alcoholates formed by methyl alcohol are called *methylates*; those formed by ethyl alcohol, *ethylates*.

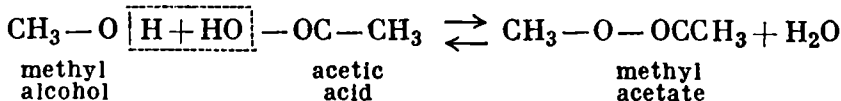
Alcoholates are solid substances readily soluble in alcohol. The sodium alcoholates are unstable compounds, which quickly darken (resinify) upon being exposed to the air, especially upon heating. Sodium methylate is the most stable. Traces of moisture cause sodium alcoholates to decompose, with the regeneration of alcohol:



The reaction of alcoholate formation provides further evidence of the similarity of alcohol and water. Metallic sodium, as is known, causes a violent evolution of hydrogen from water. The lowest alcohols CH_3-OH and $\text{C}_2\text{H}_5-\text{OH}$, which are the closest analogues of water, likewise react violently with sodium; the intermediate alcohols react less violently, while the higher react only upon heating. Alcoholates are also formed by the action of other metals, such as magnesium and aluminium.

In this reaction of alcoholate formation, alcohols exhibit acid properties, although conventional indicators fail to detect hydrogen ions in them.

2. *The substitution of radicals for the hydroxyl hydrogen with the formation of esters.* The interaction of alcohol with an organic acid produces an ester:

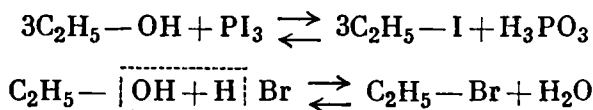


The reaction of the formation of esters is called *esterification*. Formally speaking, it is analogous to the reaction of neutralization, with the alcohol playing the part of an alkali and the ester resembling a salt. But even though alcohols do contain the hydroxyl group OH, they are not alkalis. With respect to litmus and phenolphthalein, alcohols are neutral compounds. Both alcohols and esters are, moreover, non-ionic. Therefore, the similarity between the reactions of esterification and neutralization is purely formal. Esterification is a reversible reaction: water decomposes an ester into the initial substances, acid and alcohol. This hydrolytic decomposition of esters is called *hydrolysis*.

The reaction of esterification and the resulting esters are of tremendous importance; for this reason the reaction will be considered in greater detail in a subsequent chapter (p. 234).

II. Reactions Involving the Alcohol Hydroxyl Group. The alcohol hydroxyl does not dissociate; nevertheless, in some reactions it has a certain mobility and can be replaced or detached.

1. *Replacement of the hydroxyl by a halogen with the formation of a halogen derivative of a hydrocarbon.* This reaction is ordinarily effected by subjecting alcohols to the action of halogen compounds of phosphorus or hydrogen halides (p. 104):

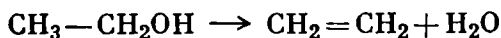


The preparation of halogen derivatives of hydrocarbons by the interaction of alcohols with hydrogen halide acids is a particular case of the reaction of esterification. As mentioned above, the compounds resulting from the alcohol-acid interaction are called esters. The halogen derivatives of hydrocarbons may therefore be regarded as esters formed by alcohols and hydrogen halide acids.

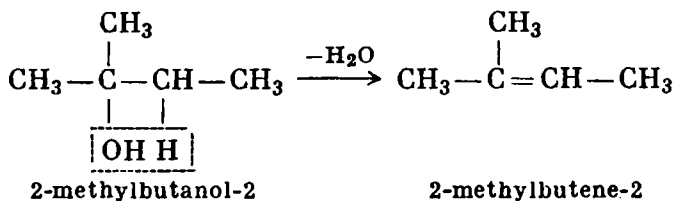
The interaction of alcohols with hydrogen halide acids is a reversible reaction, inasmuch as water decomposes the resulting alkyl halide (ethyl bromide in the above reaction) into the initial substances. To secure a bigger yield of ethyl bromide it is necessary to shift the balance from left to right, which can be achieved either by increasing the concentration of the initial substances or by removing water from the reaction mixture. In practice the reaction is conducted in the presence of dehydrating agents, such as concentrated H_2SO_4 , or else the gaseous hydrogen halide is passed into absolute alcohol. To reduce the amount of water present it is more convenient to use the hydrogen halide salt than the acid and to obtain the dry hydrogen halide from it by the action of concentrated sulphuric acid. This is the most expedient procedure, since the resulting hydrogen halide is more active when nascent.

2. *Formation of olefines by dehydration.* When an alcohol is heated with a large amount of concentrated sulphuric acid or zinc chloride, or when alcohol vapours are passed through a porcelain tube with aluminium oxide at $350-500^\circ$, the alcohol is dehydrated with the formation of ethylene hydrocarbons. Ethyl alcohol, for instance,

yields ethylene (p. 86):

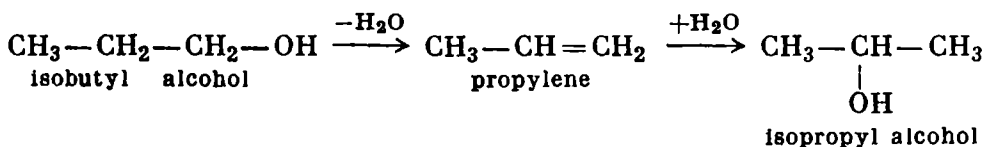


The molecule of water is formed by the hydroxyl and a hydrogen atom from a neighbouring carbon atom:

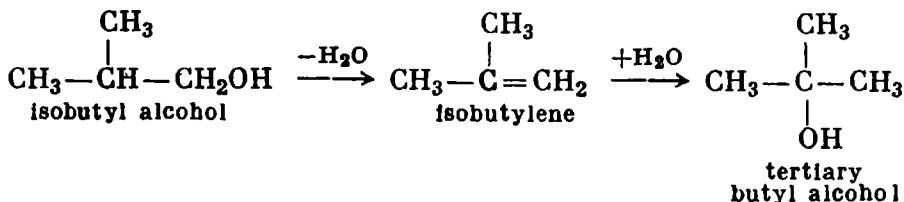


The ease with which alcohols are dehydrated increases in the order: primary, secondary, tertiary.

The reaction of ethylene hydrocarbon formation from alcohols makes it possible to convert primary alcohols into secondary or tertiary. It will be remembered that the hydration reaction obeys Markovnikov's rule (p. 77). For example, by removing water from primary propyl alcohol, we can obtain propylene, while the addition of a molecule of water to propylene will produce isopropyl alcohol:



Similarly, by removing water from isobutyl alcohol and then adding a molecule of water to isobutylene, we obtain tertiary butyl alcohol:

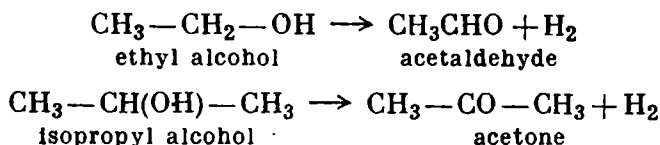


When an excess of alcohol is heated with sulphuric acid, or when alcohol vapours are passed through powdered anhydrous aluminium sulphate at 200°, ethers are formed as well as ethylene hydrocarbons (p. 167):



3. *Dehydrogenation.* When alcohol vapours are led over metals — iron, zinc, finely divided copper, etc. — at 200-300°, primary alcohols decompose into an aldehyde and hydrogen, while secondary

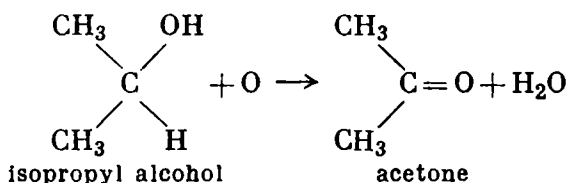
alcohols yield a ketone and hydrogen:



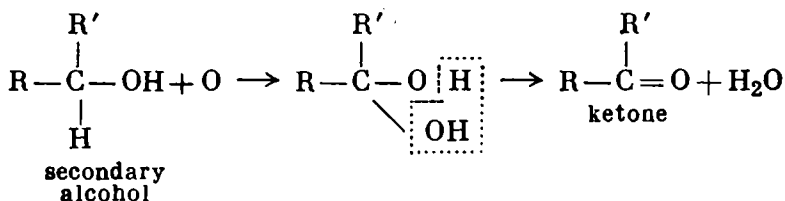
III. Alcohol Oxidation. The oxidation of alcohols is usually effected by rather strong oxidizing agents, such as $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ or $\text{KMnO}_4 + \text{H}_2\text{SO}_4$. The action of the oxidizing agent is directed at the hydroxyl-bearing carbon atom. This results in different oxidation products depending upon whether the alcohol oxidized is primary, secondary, or tertiary.

In the case of a tertiary alcohol, which has no hydrogen attached to the hydroxyl-bearing carbon atom, oxidation causes a rupture of carbon bonds. This usually produces several oxygen-containing compounds, each having fewer carbon atoms than the alcohol.

The oxidation of secondary alcohols produces *ketones* (p. 178). For instance, the oxidation of secondary propyl alcohol (isopropyl alcohol) gives *acetone*:

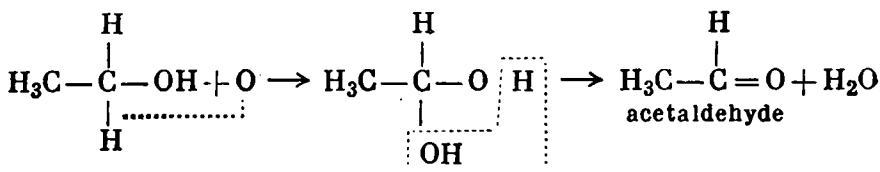


Or in general:

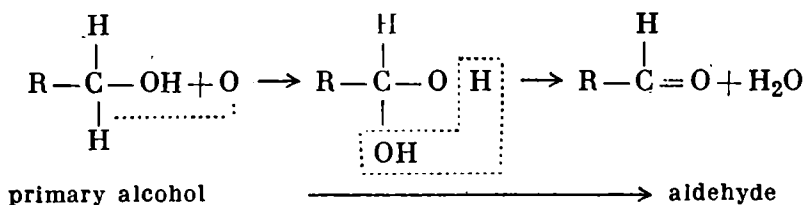


The oxidation of primary alcohols proceeds similarly, but since the hydroxyl-bearing carbon atom of a primary alcohol has one hydrogen atom more than has a secondary alcohol, the oxidation products are substances containing the $-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array}$ group and are called *aldehydes* (p. 177).

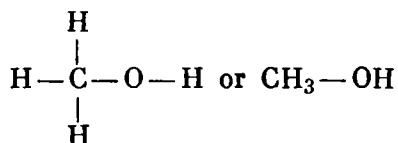
For example, ethyl alcohol upon oxidation gives acetaldehyde:



Or in general:



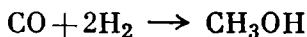
59. Principal Alcohols. Methyl Alcohol (Methanol). The structure of methyl alcohol is expressed by the formula:



Until quite recently methyl alcohol was prepared almost exclusively by the dry distillation of wood. For this reason it is also known as wood spirit.

The dry distillation of wood yields a combustible gas, consisting chiefly of CO , CO_2 , CH_4 , and H_2 , as well as charcoal and liquid products, which are divided into an oil layer (tar or pitch) and an aqueous layer, pyroligneous liquor, in which acetic acid, *methyl alcohol*, acetone, and several other substances are dissolved. This mixture is treated with $\text{Ca}(\text{OH})_2$ and divided into cuts by distillation in a special apparatus; this yields methyl alcohol containing an insignificant amount of water and volatile admixtures.

Nowadays methyl alcohol is produced for the most part synthetically: by leading a mixture of hydrogen and carbon monoxide at a high temperature and high pressure over a catalyst (zinc oxide mixed with certain other substances):



The preparation of methyl alcohol by this procedure differs radically from the wood distillation technique. In wood distillation the methyl alcohol is formed as a decomposition product of the organic substance of the wood, whereas the formation of methyl alcohol from carbon monoxide and hydrogen proceeds as its synthesis from simpler substances. Industrial syntheses of this type have lately been acquiring ever greater significance.

A most important part in modern industrial syntheses is played by *catalytic* processes.

Homogeneous and Heterogeneous Catalysis. Processes that take place under the influence of catalytic agents play a very important role in the synthesis of many organic substances both in the laboratory and in industry.

One of the first catalysts was sulphuric acid; by heating starch with dilute sulphuric acid K. Kirkhgof (St. Petersburg, 1811) converted the starch into sugar and on this basis established the industrial production of glucose. Sulphuric acid and certain other acids have a similar catalytic effect upon the reaction of the dehydration of alcohols to ethers or olefines, and also upon the reverse reaction of the hydration of these substances to corresponding alcohols. When, for instance, ethyl alcohol is added to heated concentrated sulphuric acid at a temperature of 140° , we obtain ether, while at a temperature of 170° we get ethylene. When ether or ethylene is heated with dilute sulphuric acid, we observe the reverse reaction of hydration to ethyl alcohol. No sulphuric acid is in this case expended; were it not for the side reactions of oxidation, the acid could catalyze the conversion of an infinite amount of alcohol or ether. If the catalyzed substance and the catalyst are in the same state and there is no visible interface between them (as in our example), the catalysis is called *homogeneous*, while if the catalyst is a solid substance and the reacting compounds are fluid, we have a case of *heterogeneous* catalysis. A catalyst does not accelerate any reaction, but only a reaction that is thermodynamically possible in given conditions, moreover, in the case of balanced reactions the catalyst does not shift the point of equilibrium, i.e., it accelerates the forward and the reverse reaction equally. Another characteristic feature of catalysts is their specific, or selective, effect: a catalyst will usually accelerate only one of the many possible reactions, i.e., it will be of help in preparing only one end product.

The most important homogeneous catalysts used in organic chemistry are acids, bases, aluminium chloride, alcohol aluminates, and boron trifluoride.

Highly effective and selective organic catalysts, which are tremendously important, especially in natural processes (fermentation, digestion, respiration), are various *ferments* (*enzymes*). In recent years artificially prepared organic catalysts have likewise been becoming increasingly important.

The most important heterogeneous catalysts in organic chemistry are aluminosilicates, oxides of metals (aluminium, chromium, copper, zinc, and others) and metals (platinum, palladium, nickel, copper, iron, etc.). A simple laboratory installation for the catalytic transformation of organic substances is shown in Fig. 15.

The development of an industry based on organic synthesis depends in a large measure on the successful application of this or that catalyst. Catalysis is used extensively in the chemical industries of today, specifically in the production of synthetic rubber, synthetic petrol, cooking fats, high-molecular compounds, and plastics, not to mention many others. For the catalytic cracking process see p. 68.

Fig. 16 shows an installation for the synthetic production of methyl alcohol.

A mixture of carbon monoxide and hydrogen is compressed to 120-250 atm by compressor 1 and passed through a system of filters (not shown in the picture), which removes the machine-oil traces resulting from the passage of the gas through the compressor. The mixture of gases is then fed into unit 2, where it is mixed with the unreacted gas; it then enters contact column 3, which contains the catalyst.

The contact column is a strong steel cylinder with the catalyst placed in a tube inside in such a way that there remains an annular passage between the wall of this tube and the wall of the outer cylinder. To initiate the process, the contact column is heated by elec-

tricity; afterwards the heating is discontinued, since the heat generated by the reaction is sufficient to maintain the required temperature.

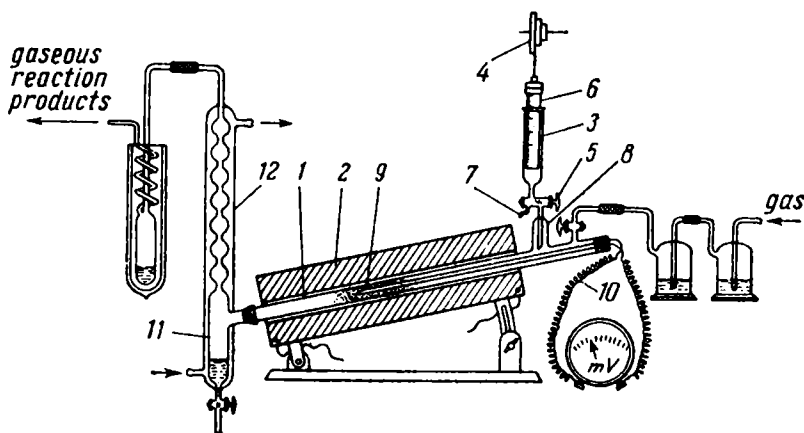


Fig. 15. Laboratory catalytic installation:

1—reaction tube of quartz glass; 2—tube furnace; 3—initial liquid injector; 4—electric motor pulley; 5—two-way cock (connected to reaction tube); 6—injector piston; 7—injector inlet for initial liquid; 8—capillary tube through which liquid trickles into reaction tube; 9—catalyst; 10—thermocouple for measuring temperature; 11—receiver; 12—cooler.

The gas rises upwards through the annular space in the contact column, heated by the reaction taking place, and then enters the inner tube. From the column the methyl alcohol vapours and the

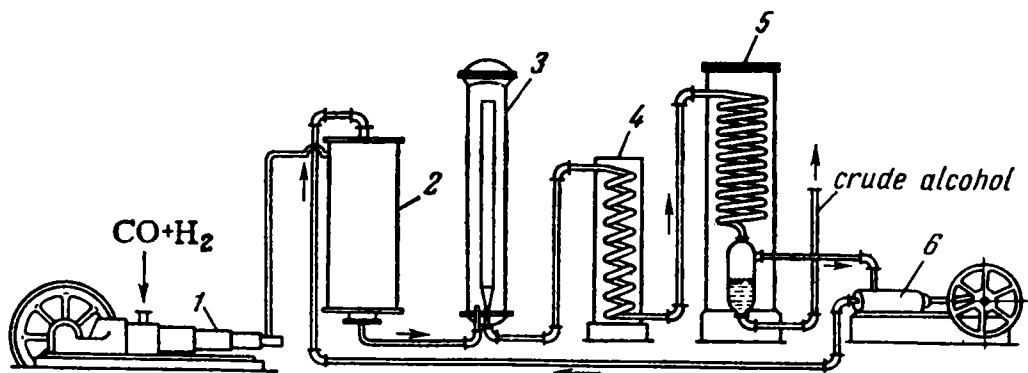


Fig. 16. Installation for the synthetic production of methyl alcohol:

1—compressor; 2—mixer; 3—contact column; 4, 5—cooling towers; 6—pump.

unreacted carbon monoxide and hydrogen go to the cooling towers 4, 5. The alcohol vapours are condensed in the reservoir of the second cooling tower and collected in the receiver. The unreacted carbon monoxide and hydrogen are returned by pump 6 (through a filter) to the contact column.

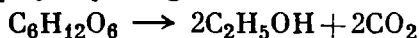
Synthetic methanol is a much purer product than methyl alcohol prepared by wood distillation, which always contains traces of acetone.

Methyl alcohol is a light (density 0.79 g/cu cm) liquid, which boils at 65° and freezes at -97°. It burns with a blue flame. When ingested even in small amounts, it causes severe poisoning accompanied by loss of eyesight. The ingestion of large amounts can be fatal. Methyl alcohol is used in the manufacture of lacquers and varnishes, in the production of formaldehyde, and as a denaturant for ethyl alcohol. In organic synthesis it serves to introduce the methyl group into molecules of various substances. It is highly important in the manufacture of dyes and various pharmaceutical compounds.

60. Ethyl Alcohol (Ethanol). Ethyl alcohol is also known as "Spirit of Wine". It is prepared in vast quantities by the fermentation of saccharoid substances.

The alcoholic fermentation of saccharoid substances is produced by yeast mould. The most favourable temperature range for fermentation is 25-30°.

Alcoholic fermentation consists in the decomposition of grape-sugar (glucose) $C_6H_{12}O_6$, by stages, into alcohol and carbon dioxide:



The famous French scientist L. Pasteur believed that fermentation depends on the presence of living yeast cells. It was his opinion that fermentation is a result of life without air, without free oxygen. Pasteur's generally accepted assumption was upset by the Russian physician M. Manasseina, who established by several experiments that even absolutely dead yeast cells are capable of causing fermentation. Twenty-six years after the publication of her paper (in 1897) the German chemist Buchner repeated her experiments and confirmed that fermentation does not necessarily require the presence of living cells. To destroy the cell walls of the yeast he ground it with sand and diatomite; by compressing this mass, he obtained from it a juice without any living cells. Nevertheless, the addition of even a tiny amount of this juice was quite effective in setting up the fermentation of a large amount of sugar. To refute the claim that fermentation is caused by "live protoplasm" in the juice, Buchner first killed the yeast with acetone and then demonstrated that the juice expressed from such yeast is not inferior in its action to juice from living cells.

It was thus established that fermentation is caused by a substance inside the yeast cells, which does not lose its activity when it is outside the cells.

This substance producing fermentation was named *zymase*. It belongs to the group of substances known as *enzymes*, or *ferments*. Enzymes are substances that are produced by living organisms and are highly potent organic catalysts.

Unlike ordinary catalysts, enzymes are in most cases highly specific and capable of influencing only certain definite forms of organic substances.

The above equation expresses only the over-all result of alcoholic fermentation. In actual fact, fermentation consists of a series

of chemical processes, which convert grape-sugar into various substances (p. 310). In all probability, each of these processes is caused by a special enzyme.

Neutral spirits, the alcohol used in the food industry, are in most cases produced from potatoes or grain. In the course of fermentation the proteins in these products are likewise decomposed and yield several impurities. The fermented mass (called wash) is distilled, yielding raw spirit, which contains *fusel oil*, volatile higher alcohols, as well as ethyl alcohol.

Repeated distillation of the raw spirit produces *rectified alcohol*, which contains 95.5% C_2H_5OH . The residue, called fusel oil, is an oily liquid consisting, for the most part, of propyl, isobutyl, and isoamyl alcohols.

Considerable amounts of ethyl alcohol are at present synthesized from ethylene (p. 130), which is obtained from natural and petroleum refinery gases; industrially this is the most advantageous method.

Alcohol produced for industrial purposes is denatured by the addition of substances that make it unfit to drink. Formalin, methyl alcohol, pyridine bases, and certain dye-stuffs are used for this purpose.

Ethyl alcohol is a mobile colourless liquid; its relative density at 0° is 0.806. It boils at 78° and solidifies at -110.5° ; for this reason it is used as a thermometric fluid in measuring low temperatures (down to -50°). It burns with a faintly luminous flame and is miscible with water in all proportions.

The content of alcohol in an aqueous mixture is determined by means of an alcoholimeter. This is a densimeter calibrated in volume percentages of alcohol content (degrees), instead of specific gravity. Some alcoholimeters are calibrated in weight percentages of alcohol content.

Alcohol is a product of great importance in the national economy. Large quantities of it are used in the manufacture of synthetic rubber. It is also used in the preparation of drugs, scents and eau-de-Cologne, the manufacture of lacquers and varnishes, smokeless gunpowder, etc.

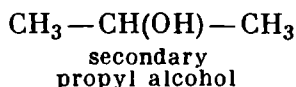
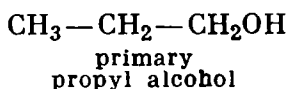
In recent years increasing quantities of alcohol have been used as petrol for internal combustion engines.

Ethyl alcohol also finds extensive application in preserving biological specimens. In many cases it is necessary to have thoroughly dehydrated, or "absolute", alcohol. Complete separation of alcohol from water cannot be achieved by simple distillation because with water alcohol forms an *azeotropic mixture*, i.e., one that cannot be separated by ordinary rectification. This mixture consists of 95.6% alcohol and 4.4% water; it boils at 78.15° (at 760 mm),.

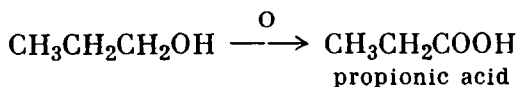
whereas absolute alcohol boils at 78.37° and water at 100° . Nor can water be removed from such a mixture by dehydration with calcium chloride because the latter combines with alcohol to form the compound $\text{CaCl}_2 \cdot 3\text{C}_2\text{H}_5\text{OH}$, which is soluble in alcohol. Almost anhydrous alcohol can be prepared by the prolonged infusing of powdered anhydrous copper sulphate (obtained by heating blue vitriol) in rectified alcohol. The salt extracts nearly all the water from the alcohol and does not dissolve in the alcohol.

The best dehydration is achieved by boiling alcohol for several hours with a large amount of calcined lime, with subsequent distillation; the distillate must be protected from exposure to moist air.

61. Propyl, Butyl, and Amyl Alcohols. In the case of *propyl alcohol* both of the theoretically possible isomers are known: primary propyl alcohol, which boils at 97° , and secondary propyl (isopropyl) alcohol, which boils at 82.4° :



The structure of the primary alcohol is confirmed by its oxidation to propionic acid:

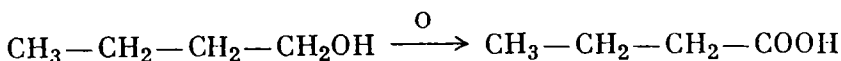


Consequently, the alcohol boiling at 82.4° is secondary.

Small quantities of the primary alcohol are contained in fusel oil. The secondary alcohol can be prepared from propylene, which is contained in petroleum cracking gases; it is used as a solvent.

Butyl Alcohols. As pointed out above, four isomers are possible for the $\text{C}_4\text{H}_9\text{OH}$ alcohols, according to the theory of chemical structure. All of them have been prepared, and their structure has been proved beyond doubt.

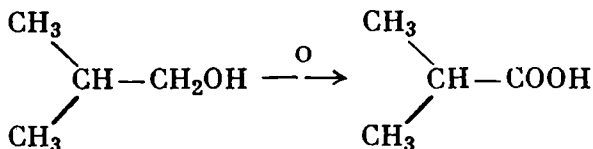
n-Butyl alcohol (butanol-1) has the highest boiling point (117.9°); 8.3 parts of this alcohol dissolve in 100 parts of water. Its oxidation produces normal butyric acid, which confirms the structure of the alcohol:



n-Butyl alcohol is at present readily available, since it is manufactured industrially by what is known as the acetobutylicum fermentation of saccharoid substances, effected by special bacteria—*Bacillus Clostridium Acetobutylicum*.

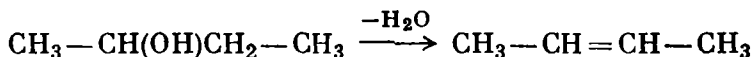
Isobutyl alcohol (2-methylpropanol-1) has been known for a long time, as it is a product of the distillation of fusel oil, obtained in alcoholic fermentation (p. 142). Oxidation turns it into isobutyric

acid—hence, it is a primary alcohol:



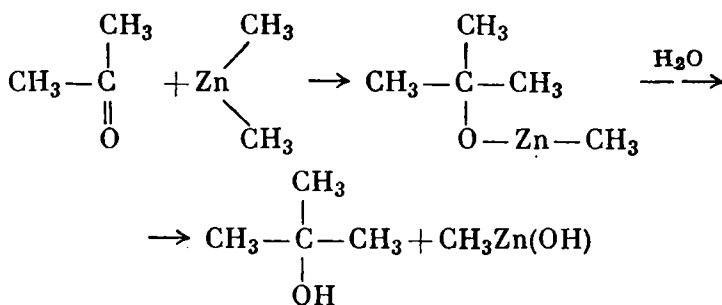
Isobutyl alcohol has a relatively low solubility in water.

Secondary butyl alcohol (butanol-2) can be dehydrated to butene-2:



Oxidation turns butanol-2 into the corresponding ketone (methyl ethyl ketone $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CH}_3$); this establishes the structure of butanol. It is used in the form of esters of acetic, butyric, and other acids in making fruit essences and certain scents (artificial musk), as well as certain drugs.

Tertiary butyl alcohol (2-methylpropanol-2, trimethylcarbinol) was obtained by Butlerov in 1864 by the action of dimethylzinc on acetone:



Upon cooling, trimethylcarbinol crystallizes (m.p. 25.5°); it has a lower boiling point (83°) than its isomers, is completely miscible with water, and has an odour of camphor.

Amyl Alcohols. As mentioned above (p. 128), eight isomers are known for the alcohol with five carbon atoms (see table on p. 145).

These are known as the *amyl alcohols*.

The amyl alcohols are manufactured commercially from petroleum cracking gases.

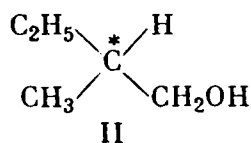
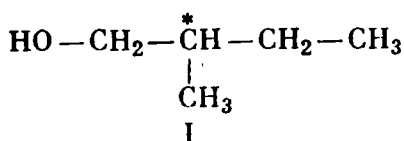
The amyl fraction of fusel oil contains mostly isoamyl alcohol, 2-methylbutanol-4 (IV), with an admixture of the optically active 2-methylbutanol-1 (VII). Commercial isoamyl alcohol (often called simply "amyl alcohol") has a characteristic odour; inhalation of its vapours irritates the throat and causes coughing. Amyl alcohol has a low solubility in water (2 parts in 100 parts of water).

It is used as a solvent and in the production of organic acid esters, which find application as essences, e.g., isoamyl-acetate, or pear essence.

Amyl Alcohol Isomerism

Carbon skeleton isomerism	Hydroxyl position isomerism	Isomer formula
$\begin{array}{c} 5 & 4 & 3 & 2 & 1 \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \end{array}$	$\text{I} \quad \begin{array}{c} 5 & 4 & 3 & 2 & 1 \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{OH} \end{array}$	$\begin{array}{c} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_2 & \text{OH} \\ \text{pentanol-1} \end{array}$
	$\text{II} \quad \begin{array}{c} 5 & 4 & 3 & 2 & 1 \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & \text{OH} \end{array}$	$\begin{array}{c} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}(\text{OH}) & - & \text{CH}_3 \\ \text{pentanol-2} \end{array}$
	$\text{III} \quad \begin{array}{c} 5 & 4 & 3 & 2 & 1 \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & \text{OH} \end{array}$	$\begin{array}{c} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & - & \text{CH}_2 & - & \text{CH}(\text{OH}) & - & \text{CH}_2 & - & \text{CH}_3 \\ \text{pentanol-3} \end{array}$
$\begin{array}{c} \text{C} \\ \\ 1 & 2 & 3 & 4 \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \end{array}$	$\text{IV} \quad \begin{array}{c} \text{C} \\ \\ 1 & 2 & 3 & 4 \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{OH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ 1 & 2 & 3 & 4 \\ \text{CH}_3 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH} \\ \text{2-methylbutanol-4} \end{array}$
	$\text{V} \quad \begin{array}{c} \text{C} \\ \\ 1 & 2 & 3 & 4 \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & \text{OH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ 1 & 2 & 3 & 4 \\ \text{CH}_3 & - & \text{CH} & - & \text{CH}(\text{OH}) & - & \text{CH}_3 \\ \text{2-methylbutanol-3} \end{array}$
	$\text{VI} \quad \begin{array}{c} \text{C} \\ \\ 1 & 2 & 3 & 4 \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & \text{OH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ 1 & 2 & 3 & 4 \\ \text{CH}_3 & - & \text{C} & - & \text{CH}_2 & - & \text{CH}_3 \\ & & \text{OH} \\ \text{2-methylbutanol-2} \end{array}$
	$\text{VII} \quad \begin{array}{c} \text{C} \\ \\ 1 & 2 & 3 & 4 \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & \text{OH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HOH}_2\text{C} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_3 \\ \text{2-methylbutanol-1} \end{array}$
$\begin{array}{c} \text{C} \\ \\ 3 & 2 & 1 \\ \text{C} & - & \text{C} & - & \text{C} \\ & & \\ & & \text{C} \end{array}$	$\text{VIII} \quad \begin{array}{c} \text{C} \\ \\ 3 & 2 & 1 \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{OH} \\ & & \\ & & \text{C} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ 3 & 2 & 1 \\ \text{CH}_3 & - & \text{C} & - & \text{CH}_2 & \text{OH} \\ & & \\ & & \text{CH}_3 \\ \text{2,2-dimethylpropanol-1} \end{array}$

62. Optical Activity of Organic Compounds. Some of the alcohols exhibit a rather remarkable type of isomerism. This is illustrated by 2-methylbutanol-1 (I), which it is more convenient to represent by formula II:



Two isomers are known for this amyl alcohol; their molecules have the same structure, expressed by the above formula. In all their chemical and most of their physical properties the two isomeric alcohols are indistinguishable. Their relative densities, boiling points, indices of refraction, etc., are absolutely identical. One property alone distinguishes them: when polarized light is passed through them, one of them rotates the plane of polarization to the right, while the other rotates that plane through the same angle to the left.

Some solids, such as quartz and lithium potassium sulphate, are capable of rotating the plane of polarization of a beam of light, but only in the crystalline state. These substances form crystals that

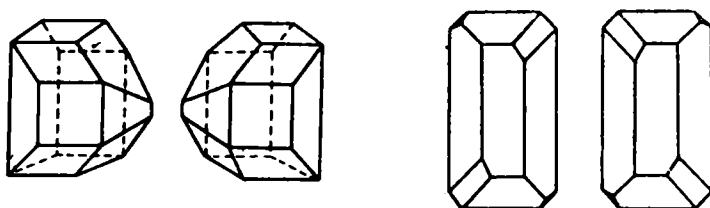


Fig. 17. Enantiomorphic crystals.

are mirror images of one another and are non-superposable. In other words, their relation to one another is that of an object without a plane of symmetry to its image in the mirror. This is the same relationship as that between the shape of the right hand and the left, or between similar spirals turned in opposite directions. Crystals of this kind are called *enantiomorphic* (Fig. 17). One of the two enantiomorphs rotates the plane of polarization of a polarized beam of light to the right; the other, to the left. If the crystalline structure of such bodies is destroyed by dissolving or melting them, they lose their rotating ability. The ability thus depends on the structure of the crystal, not on the structure of the molecules themselves.

The rotating ability of the amyl alcohols is quite different: they are optically active even in solution, as well as in the vapour state. Consequently, their optical activity can be traced to the structure of their molecules.

In the amyl alcohol molecule the carbon atom marked in the formulas above by an asterisk is linked by one bond to an ethyl group, by another bond to a hydrogen atom, by a third bond to a methyl group, and by the fourth to a CH_2OH group. One of the carbon atoms in amyl alcohol is in this way connected with four *different* groups of atoms; it is called an *asymmetric carbon atom*.

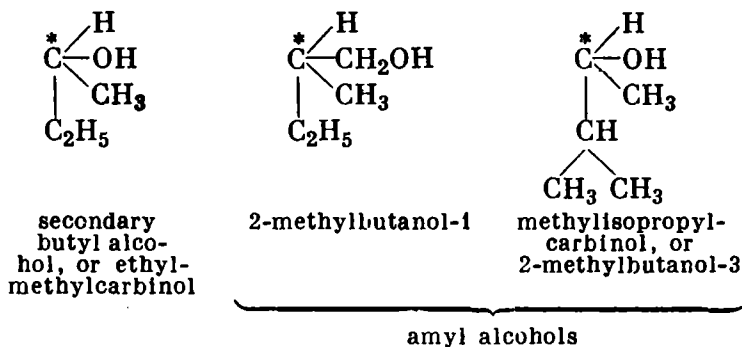
J. van't Hoff in 1874 established that the presence of an asymmetric carbon atom in the molecule is a sufficient cause for an organic substance to be optically active.

J. H. van't Hoff, a Dutch chemist (1852-1911), was one of the founders of stereochemistry and modern physical chemistry. Up to 1895 he worked in Holland (Utrecht and Amsterdam) and after that in Germany (Berlin).

His famous paper on stereochemistry, "The Position of Atoms in Space", was published when he was still very young (22-23 years old). It contained bold ideas on asymmetric carbon atoms, accounting for the optical activity of organic compounds. Similar views were published at the same time by the French chemist J. A. Le Bel. The work of these two scientists laid the foundations of the stereochemistry of organic compounds.

Van't Hoff later turned his attention to physical chemistry—to chemical dynamics, the theory of chemical equilibrium, the study of salt solutions, the laws governing osmotic pressure, and many other subjects.

The following are examples of optically active organic compounds:



All these compounds contain an asymmetric carbon atom, designated in the structural formulas as C^* .

It is obvious that if a halogen atom is substituted for the hydroxyl group in these alcohols, the resulting halogen derivatives will likewise contain asymmetric carbon atoms.

It should be borne in mind that when these alcohols are prepared synthetically from optically inactive compounds, an equal number of "left" and "right" molecules is formed. The rotation of some is thus compensated by the reverse rotation of others, and the substance as a whole does not exhibit any optical activity. This is considered in greater detail on p. 149.

Optical Activity Measurement. The optical activity of organic compounds is measured by means of instruments called *polarimeters*.

The simplest polarimeter (the so-called half-shadow polarimeter) is depicted in Fig. 18. The beam of light from source 1 passes through the rigidly mounted Nicol prism 2 (*the polarizer*), emerging from it in a polarized beam. The beam then strikes the second Nicol prism 3 (*the analyzer*), which can be turned by means of rotator 4; finally, through lens 5 it reaches the observer's eye. The instrument is adjusted so that if the beam does not pass through an optically active substance between the polarizer and the analyzer, the analyzer must be in zero position for the observer to see two equally illuminated halves of a circular field in the eyepiece. If, however, the long glass tube 6 filled with an optically active substance is

placed between the polarizer and the analyzer, the plane of polarization of the beam of light changes by some angle, and one of the halves becomes lighter than the other. The analyzer 2 is now turned until both halves of the circular field are again illuminated equally. The angle through which the analyzer was turned (determined from the reading on the circular graduated scale 7) gives the angle through which the plane of polarization of the beam of light is rotated when

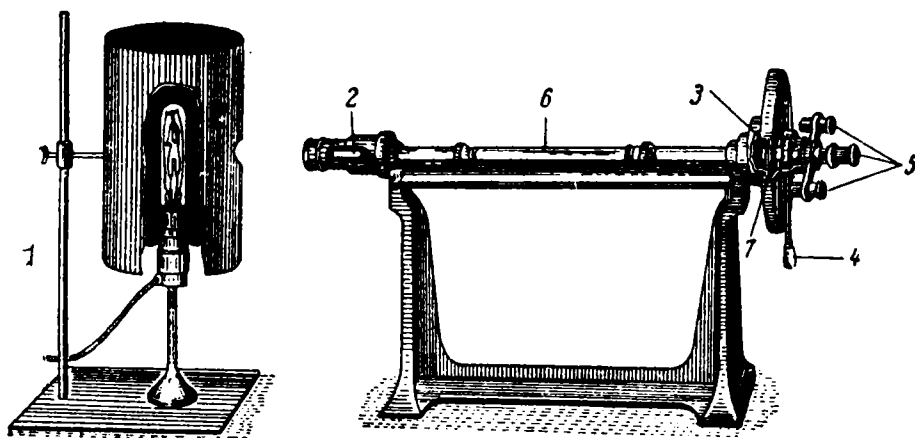


Fig. 18. The half-shadow polarimeter:

1—light source; 2—polarizer; 3—analyzer; 4—rotator; 5—lens; 6—tube containing substance; 7—circular graduated scale.

the beam passes through the investigated substance, i.e., it gives the value of the substance's optical activity.

This value depends on the temperature, the wavelength of the polarized light used, and the nature of the solvent. It is directly proportional to the thickness of the latter and (in most cases) to the concentration.

For quantitative comparisons of the optical activity of different substances, it is necessary to calculate the so-called *specific rotation*. This is the angle of rotation for a layer of liquid 1 dm thick and a concentration of the optically active substance equal to 1 g/ml. The specific rotation is designated as $[\alpha]$. If a 100 ml solution containing c grams of a substance (the layer thickness being L decimeters) rotates the plane of polarization of a beam of light through an angle α , the specific rotation

$$[\alpha] = \frac{\alpha \cdot 100}{L \cdot c}$$

But if an optically active liquid, whose relative density is d , is taken undiluted, the specific rotation is calculated according

to the formula:

$$[\alpha] = \frac{\alpha}{L \cdot d}$$

The temperature at which the measurement was taken and the wavelength of the light should, of course, be indicated in this case. Rotation to the right (dextrorotation) is denoted by a plus sign; rotation to the left (laevorotation), by a minus sign. If, for instance, the specific rotation of the optically active amyl alcohol contained in fusel oil and measured at 20° for the *D* line of the solar spectrum (wavelength 589 mμ) is 5.9° to the left, this may be written as follows:

$$[\alpha]_D^{20} = -5.9^\circ$$

Rotation usually increases markedly with the transition to the shorter wavelengths of light. Instruments making it possible to determine and record the rotation throughout the entire visible and ultraviolet part of the spectrum, i.e., from 220 to 780 mμ, are called *spectropolarimeters*. The curves of rotation dispersion obtained in this way provide a much more comprehensive picture of the optical activity of a substance.

63. Stereochemical Theory. The ordinary structural formulas of the amyl alcohol isomers, which depict the molecule as if situated in a plane, furnish no explanation of the optical isomerism exhibited by these alcohols. The phenomenon does, however, become easily understandable, if the atoms, which make up the molecule are assumed to have a spatial arrangement.

As far back as 1863 Butlerov wrote: "If atoms really exist, I see no reason why all attempts to determine their spatial arrangement should necessarily be futile, why the future should not teach us to make such determinations."

In 1874 van't Hoff and Le Bel laid the groundwork of stereochemistry, i.e., the theory of the arrangement in space of the atoms in a molecule. According to van't Hoff's theory, the valency bonds of a carbon atom are directed towards the vortices of a regular tetrahedron with the carbon in its centre. This model supplies a satisfactory interpretation of the equivalence of all four bonds of the carbon atom, since the most symmetric configuration of four points in space around a fifth is that in which the four points are in the vortices of a regular tetrahedron, while the fifth is in its centre*. The directions of the valency bonds thus coincide with the lines connecting the centre of the regular tetrahedron with its vortices and are at angles of 109°28' to one another.

* The centre of a regular tetrahedron is situated on a perpendicular dropped from the vortex to the base, at a distance of one quarter of the perpendicular from the base. This is the point of intersection of the altitudes of a regular tetrahedron.

When all four valency bonds of the carbon atom are saturated by different atomic groups, the groups, as shown in Figs. 19 and 20, can be arranged in two different ways. In Fig. 19 this is shown by tetrahedra; in Fig. 20, merely by the direction of the valency bonds.

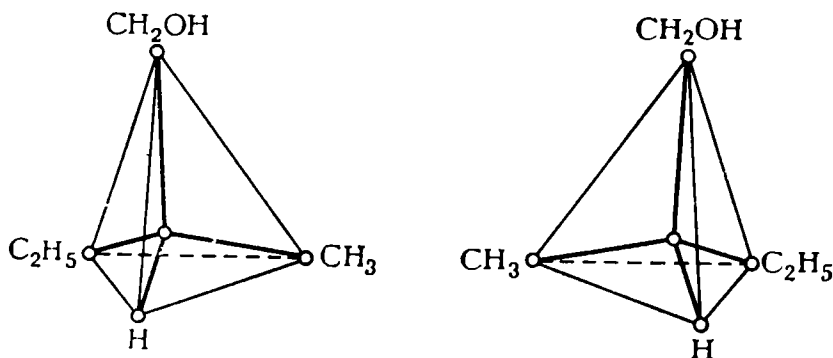


Fig. 19. Spatial configuration of radicals and atoms in molecules of dextrorotating and laevorotating amyl alcohols.

It is not hard to see that the first configuration is the mirror image of the second and that they cannot be superimposed one on the other.

The difference between them becomes especially clear if we go mentally from the CH_2OH group via H to C_2H_5 . In one case the movement is clockwise; in the other, counter-clockwise.

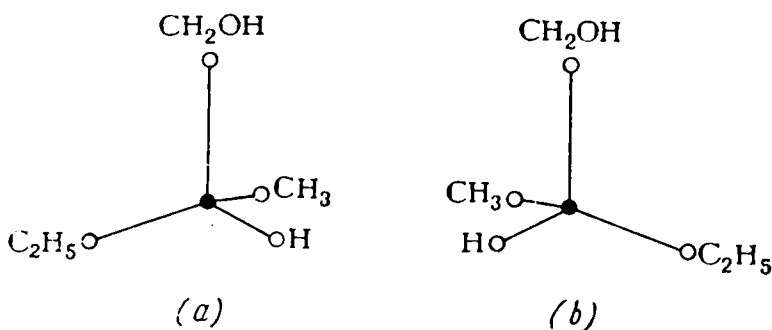


Fig. 20. Directions of valency bonds of radicals and atoms in molecules of dextrorotating and laevorotating amyl alcohols.

The difference between dextrorotating amyl alcohol and the laevorotating isomer may thus be traced to the asymmetry of their molecules: since they contain an asymmetric carbon atom, the molecules have no plane of symmetry. Isomers like dextrorotating and laevorotating amyl alcohols are called *optical antipodes*. A model of the molecule of one of the antipodes is the mirror image of a model of the molecule of the other. One of the antipodes rotates

the plane of polarization of a beam of light to the right to the same extent that the other rotates it to the left.

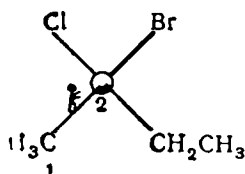
When equal amounts of dextrorotating and laevorotating amyl alcohols are mixed, we obtain inactive amyl alcohol, which has no effect on polarized light. This alcohol consists of an equal number of right- and left-hand isomers. Such mixtures of compounds are called *racemic*.

Since optical antipodes rotate the plane of polarization towards the right or else towards the left, they are sometimes called "right isomer" and "left isomer". Actually, this is incorrect, for the direction and magnitude of the rotation depend upon the solvent, the pH of the solution, and other factors. Mirror isomers can therefore best be visualized in terms of models of their molecules.

Imagine a pair of chairs: chair A has a broken front left leg; chair B, a broken front right leg. Naturally, when we say "right" and "left" in this case, we are speaking from the point of view of an observer whom we have mentally seated in the chairs. The legs of a chair as such cannot of course be either "right" or "left". This technique of describing asymmetric objects from the standpoint of an observer situated in a definite manner with respect to the object it employed quite frequently: it is applied to the banks of rivers with respect to the direction of the current, to clockwise and counter-clockwise rotation, etc.

A spatial model of the molecule of one of the antipodes is, like a broken chair, neither "left" nor "right", but it too can be given such a designation by means of the "observer technique".

Let us imagine, for this purpose, an observer walking along the carbon chain of one of the antipodes from C(1) to C(2) in 2-chloro-2-bromobutane:



The Cl atom is to the left, and the Br atom to the right, of the observer. Let us denote the position on the right by the Greek letter sigma σ and the position on the left by the Greek letter rho ρ .

Evidently, in this and similar cases a spatial structure can be described simply by designating one of the substituents by ρ or σ : 2 ρ -chloro-2-bromobutane or 2-chloro-2 σ -bromobutane.

This rule is easily applied to the mirror isomers of amyl alcohol in Fig. 20. The (a) isomer then becomes 2 ρ -methylbutanol-1, while the (b) isomer becomes 2 σ -methylbutanol-1.

Van't Hoff's theory of the tetrahedral distribution of the carbon atom bonds in molecules of the fatty compounds received experimental confirmation in the later work of Bragg, who investigated the passage of X-rays through diamond crystals. The investigation revealed that the crystal lattice of diamond is constituted in such a way that each carbon atom is in the centre of a regular tetrahedron, with other carbon atoms in its vortices (Fig. 21).

Isomerism due to the spatial configuration of the atoms in a molecule is called spatial isomerism, or *stereoisomerism*.

It should be mentioned that if a molecule of a substance contains two or more asymmetric carbon atoms, the phenomenon becomes

much more complex and the number of stereoisomers increases considerably; moreover, there is also the possibility of stereoisomers other than optical antipodes appearing.

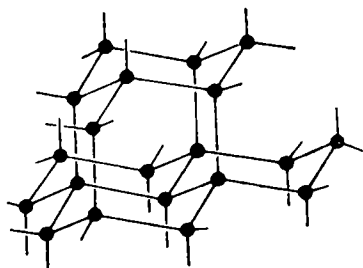


Fig. 21. Crystal lattice of diamond.

Stereochemical concepts do not conflict in any way with the theory of chemical structure. N. Zelinsky pointed out that "...no sooner were structural formulas given a stereometric meaning than that which had, seemed incomprehensible acquired new and clear contours; far from

undermining the foundations of the structural theory, this is advancing and perfecting it".

The stereochemical theory is thus a further development of the idea that forms the cornerstone of the structural theory, the idea of the bonds between atoms.

Carbon Chain Configuration. If a molecule (say, of ethane) contains two linked carbon atoms, they must be represented by two tetrahedra with a common vortex, with the line connecting their centres passing through that vortex (Fig. 22). Similarly, only one configuration is possible for the triple-link carbon chain (Fig. 23). For a chain of four or five carbon atoms, provided all of them lie in one plane, two configurations are possible: a chelate (claw-like) configuration (Figs. 24a,b) and a zigzag configuration (Fig. 24c). But if the carbon atoms are assumed to be non-planar, the number of possibilities increases infinitely.

A zigzag configuration is possible for a carbon chain of any length, whereas a chelate configuration becomes impossible for a carbon chain consisting of more than five atoms, because six carbon atoms begin to obstruct one another spatially (Fig. 25). It follows from the aforesaid that even in a normal carbon chain the atoms are not situated in a straight line.

It is noteworthy that in the crystalline state organic compounds (hydrocarbons, alcohols, acids) of normal structure contain long carbon chains of zigzag shape. This has in several cases been confirmed experimentally.

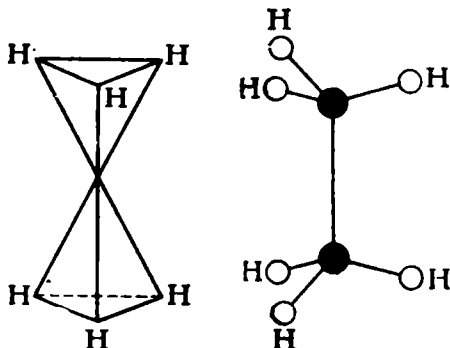


Fig. 22. Ethane molecule configuration.

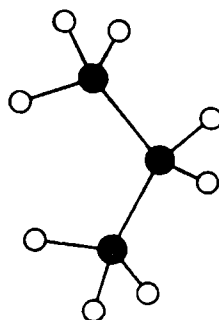


Fig. 23. Configuration of a chain of three carbon atoms.

For instance, the X-ray investigation of crystals of lauric acid $\text{CH}_3-(\text{CH}_2)_{10}-\text{COOH}$ has shown that the carbon atoms in this molecule form a zigzag, the angle of the zigzag being very close to $109^\circ 28'$, i. e., the angle between the valency bond directions in van't Hoff's tetrahedron model (Fig. 26).

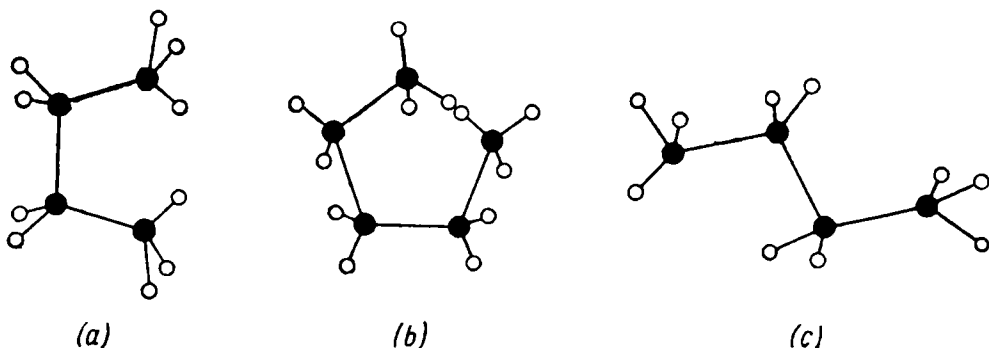


Fig. 24. Configuration of a chain of four and five carbon atoms:
a and b—chelate; c—zigzag.

64. Electronic Structure of Single Bonds (σ -Bonds). The problem of the nature of the chemical bond is one of the most complicated in organic chemistry.

As far as typical inorganic compounds are concerned, they were interpreted at various stages in the history of chemistry with great success and relative simplicity by electrostatic theories: Berzelius's theory of electrochemical dualism and the theory of electrolytic dissociation, which has in some measure remained valid to this day.

But formidable and often insurmountable difficulties and contra-

dictions were encountered wherever it was necessary to account for the formation of links between identical atoms. And it is links of this kind that prevail in organic compounds.

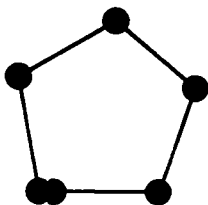


Fig. 25. Configuration of a chain of six carbon atoms.

The Lewis-Langmuir theory of the electronic structure of homoeopolar bonds constitutes a definite milestone in the evolution of our understanding of the structure of matter. The theory is based on the notion that every bond is effected by an electron pair situated between the combining atoms and shared by them in equal measure (p. 62).

These notions continue to be in use in organic chemistry to the present day.

Modern physics has added to our knowledge of the structure of covalent bonds. We know that the two electrons participating in a single chemical bond are travelling at tremendous speeds.

The swift movement of a luminous or illuminated sphere in one direction is perceived by the human eye as a bright band. If the movement of such a body is in different directions within a definite volume, the volume appears to the eye to be filled with a luminous cloud. The cloud has a non-uniform density: the regions most frequented by the electron seem more "opaque". This is a simple visual model of the "electron cloud" and of "electron density".

How are we to interpret chemical bonds in the simplest organic molecules in the light of the latest findings concerning the structure of matter?

To what extent does modern physics confirm or refute earlier ideas concerning the structure of matter?

What new and valuable ideas are suggested to organic chemists by conclusions drawn from the contemporary theory of chemical bonds?

The sole electron in the hydrogen atom travels around the nucleus (proton), forming a spherical electron cloud (Fig. 27).

However, it is only in the simplest case that the electron cloud can be spherical. A carbon atom has 6 electrons, of which only the outer 4 take part in forming covalent bonds.

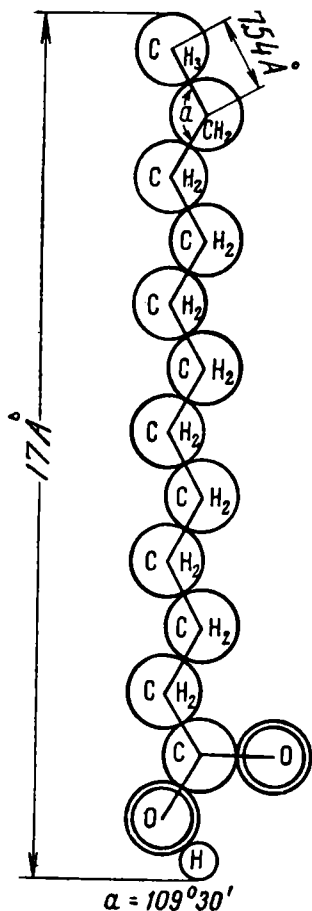


Fig. 26. Model of lauric acid molecule.

In accordance with the concepts of classic organic chemistry, it is assumed that in the simplest cases (e.g., in methane and the other saturated hydrocarbons) these four electron clouds are identical; they have the shape of asymmetric figures (Fig. 28) and are

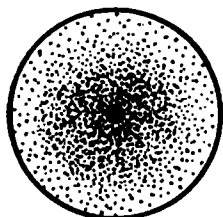


Fig. 27. Electron cloud of hydrogen atom.

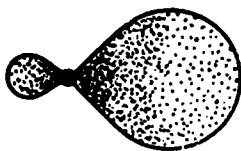


Fig. 28. Electron cloud of carbon atom.

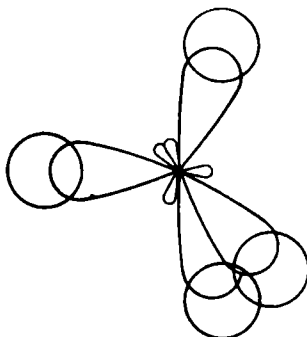
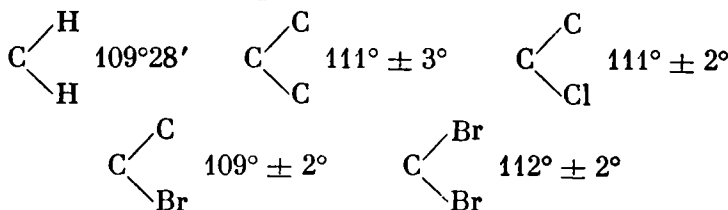


Fig. 29. Structure of methane molecule.

uniformly arranged around the carbon nucleus at angles of $109^{\circ}28'$ (Fig. 29). The carbon valency angles can alter slightly, depending on mutual attraction or repulsion between the atoms:



The angles between the valency bonds thus alter somewhat depending on the nature of the elements, but do so within relatively narrow limits.

By means of physical methods (X-ray structural analysis, etc.) it is possible to determine the absolute distances between atoms (in Ångström units; $1 \text{ Å} = 1 \times 10^{-8} \text{ cm}$).

In the methane molecule the hydrogen atoms are held by the carbon atom by virtue of the fact that the hydrogen and carbon electrons, travelling along their orbits, are attracted (although in different measure) by the nuclei of both elements. The electron clouds partly "overlap". The same applies to the C—C single bond (Fig. 30). Chemical bonds of this type are called σ -bonds (sigma bonds).

The electronic structure of an ethane molecule is represented in Fig. 31. It is evident that in ethane there are six C—H σ -bonds and one C—C σ -bond.

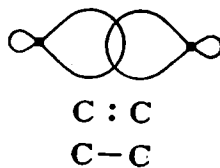


Fig. 30. Single C—C sigma bond.

Single bonds denoted by a line in structural formulas are effected by a pair of electrons, each of which travels in its own orbit.

When two different atoms combine, the electron clouds of the valency electron pair shift towards the more electronegative element; this can be designated by an arrow (Fig. 32).

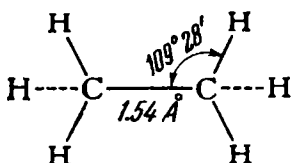
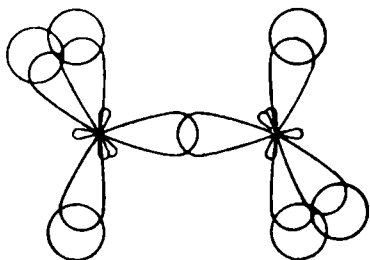


Fig. 31. Structure of ethane molecule.

The latest findings concerning the nature of the chemical bond corroborate the basic notions of classic organic chemistry regarding the direction of valency bonds,

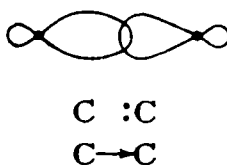


Fig. 32. Shift of electron clouds of valency electron pair.

valency angles, the circular symmetry of the single bond, and the possibility of free rotation about this bond.

Electronic notions, moreover, supplement the structural theory and elaborate upon it. This will become particularly evident when we consider the halogenated acids (p. 259), unsaturated compounds (pp. 226-29), and aromatic compounds (pp. 392, 407).

UNSATURATED ALCOHOLS

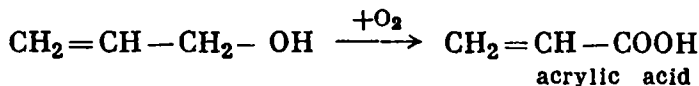
The substitution of a hydroxyl group for a hydrogen in hydrocarbons of the C_nH_{2n} unsaturated series gives rise to *unsaturated alcohols*.

65. Allyl Alcohol. The simplest of the unsaturated alcohols would appear to be vinyl alcohol $CH_2=CH(OH)$, but in reality alcohols with a hydroxyl attached to a carbon atom doubly bound to another carbon atom can exist only in exceptional conditions. Alcohols of this type undergo an isomeric transformation the moment they are formed; therefore whenever a reaction could be expected to produce the $CH_2=C(OH)-$ group, the latter experiences a rearrangement to CH_3-CO- (Eltekov's Rule). Acetaldehyde $CH_3-C \begin{smallmatrix} \nearrow O \\ \searrow H \end{smallmatrix}$

is thus formed instead of vinyl alcohol $CH_2=CH(OH)$.

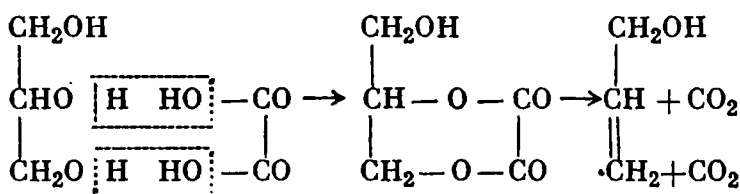
The simplest representative of the unsaturated alcohols is allyl alcohol $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ (in the Geneva nomenclature propene-1-ol-3).

The structure of allyl alcohol is confirmed by its oxidation to acrylic acid:



Allyl alcohol is a liquid (b.p. 97°) with a pungent odour; it is readily soluble in water.

Allyl alcohol occurs in pyroligneous liquor, which is obtained in the dry distillation of wood. It can be prepared by heating glycerol with formic or oxalic acid. An ester is formed as an intermediate product, and this on heating decomposes with the evolution of carbon dioxide:



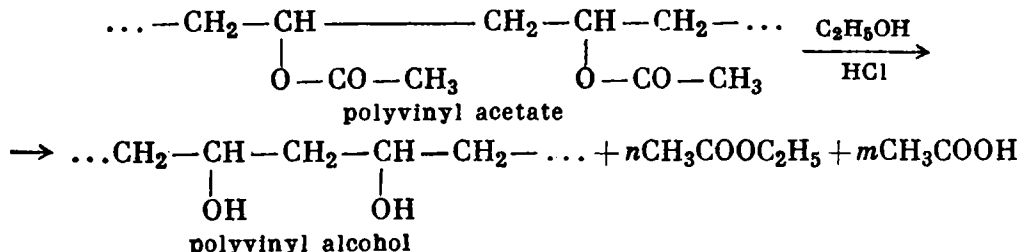
The chemical reactions of allyl alcohol are influenced by the presence both of a hydroxyl group and of a double bond.

When, for instance, allyl alcohol is subjected to the action of phosphorus trichloride or tribromide, allyl chloride $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$ or allyl bromide $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$ is formed respectively. Polymerization is an example of a reaction due to the double bond in allyl alcohol.

66. Plastics Based on Polymers of Vinyl Alcohol and Its Derivatives. Although vinyl alcohol is highly unstable, its derivatives form polymers comparatively readily, and these have many industrial applications.

Polyvinyl alcohol is prepared commercially by the saponification (hydrolysis) of polyvinyl acetate, an ester of polyvinyl alcohol, in an alcoholic solution.

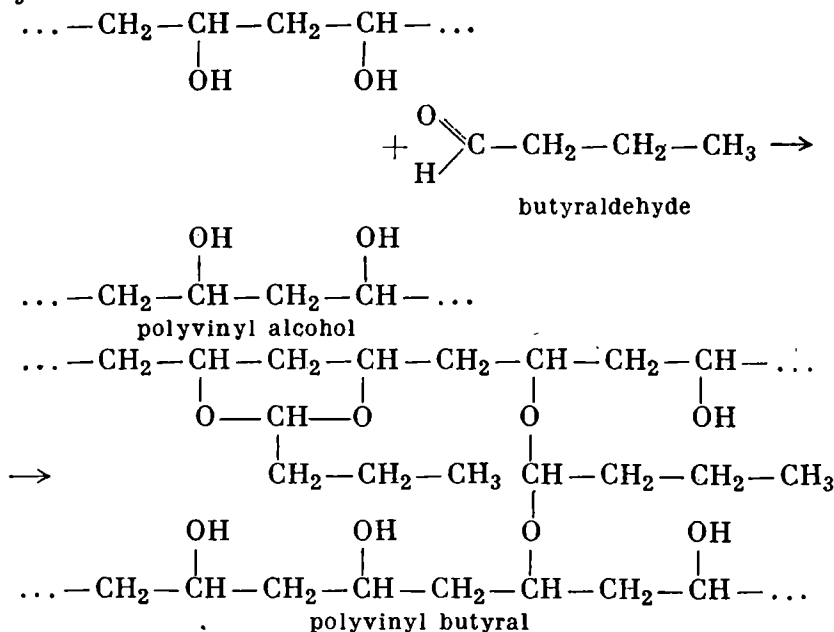
Saponification can be effected by either acids (HCl , H_2SO_4) or alkalis:



In the course of saponification the polymer becomes less soluble in alcohol and is precipitated, depending on reaction conditions, either as a fine colourless powder, or as threads, or as a gel-like mass. Polyvinyl alcohol is odourless, non-toxic, soluble in water, acids, glycerol, and glycol, and insoluble in monohydroxy alcohols, ketones, and ethers. It is one of the most water-soluble polymers.

Thanks to its water-solubility, polyvinyl alcohol is used in surgery to make threads for suturing wounds. When the wound has healed, the thread is gradually dissolved by the organism. The products of the reactions between polyvinyl alcohol and aldehydes are highly adhesive and have found extensive application as glues, electric insulation enamels, finishes, etc.

The reaction between polyvinyl alcohol and butyraldehyde produces *polyvinyl butyral*:



Polyvinyl butyral is used to make all-purpose glues and the interlayer in safety glass for motor cars and aircraft.

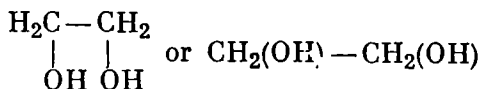
POLYHYDROXY ALCOHOLS

Dihydroxy Alcohols, or Glycols

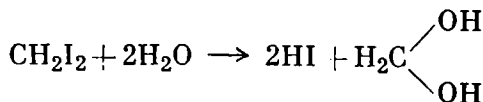
If two hydrogen atoms in saturated hydrocarbons are replaced by hydroxyls, we get *dihydroxy alcohols*, or *glycols*.

67. Structure, Isomerism, and Nomenclature of Glycols. The first representative of the group of dihydroxy alcohols, glycol, was prepared by A. Wurtz in 1856 by the hydrolysis of dichloroethane.

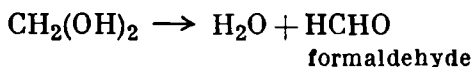
The chemical structure of this compound corresponds to the formula:



In 1861 Butlerov attempted to prepare the simplest dihydroxy alcohol by the hydrolysis of methylene iodide:

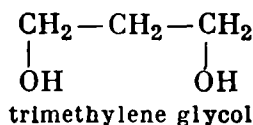
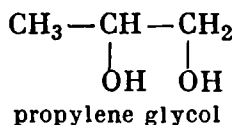


It turned out, however, that such glycols do not exist in the free state. The moment they are formed they give up water to become aldehydes or ketones:

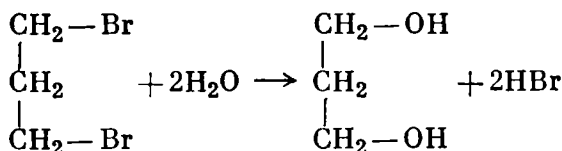


This is a property common to all organic compounds: the carbon atom can hold only one hydroxyl, substances with two hydroxyls attached to a single carbon atom are highly unstable and decompose, yielding water.

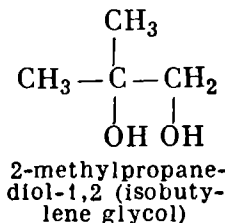
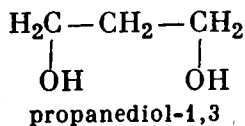
By introducing two hydroxyls into the propane molecule $\text{CH}_3\text{—CH}_2\text{—CH}_3$, we obtain two isomeric dihydroxy alcohols:



These structural formulas are confirmed by the preparation of these glycols from halogen derivatives in which the halogen atoms are attached to different carbon atoms. For instance, when trimethylene bromide is boiled with water in the presence of potash and soda, we obtain trimethylene glycol:



Since most of the dihydroxy alcohols were originally prepared by the hydrolysis of dihalogen compounds obtained from olefines, the glycols were given names based on corresponding unsaturated hydrocarbons, such as ethylene glycol and isobutylene glycol. In the Geneva nomenclature the names of the dihydroxy alcohols are formed in the same way as the names of the monohydroxy alcohols, but with the ending *diol* and with figures indicating the positions of the hydroxyls:



68. Physical and Chemical Properties of Glycols. Most of the glycols are viscous, colourless, low-volatile liquids. They are miscible with water and alcohol. Most of them have a sweet taste, but some are rather bitter.

Glycols boil at a higher temperature and have a higher relative density than corresponding monohydroxy alcohols. Ethyl alcohol, for example, boils at 78° and has a relative density of 0.806, whereas for ethylene glycol the figures are 197° and 1.109 respectively.

Glycols enter into all the reactions that monohydroxy alcohols enter into, with the sole difference that either one or both alcoholic groups can be made to participate in the reaction. For this reason the glycols have two series of derivatives: mono- and di-derivatives.

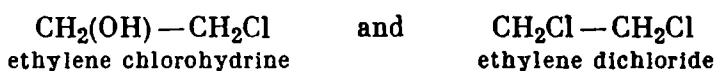
The action of metallic sodium upon glycol thus produces the glycolates:



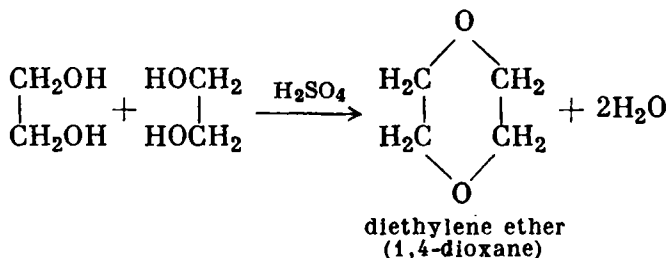
It should also be noted that the hydrogen in the glycols is more easily replaceable than the hydrogen in the alcohols.

The hydroxyls in the glycols, just as in the monohydroxy alcohols, can be replaced by halogen atoms.

The substitution of chlorine in glycol yields:

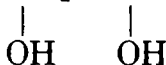


As demonstrated by A. Favorsky, the heating of ethylene glycol with small amounts of sulphuric acid removes two molecules of water from two glycol molecules, which form *dioxane*, a cyclic ether:



Dioxane is a liquid boiling at 101.2° . Large amounts of it are used as a solvent, which is miscible with water and many other organic solvents.

Ethylene glycol CH_2-CH_2 is used extensively in industry as

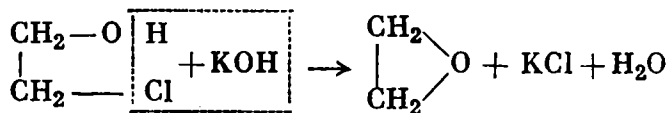


a substitute for glycerol, especially in the manufacture of anti-freezes, i.e., substances added to water to prevent its freezing. Anti-freezes are used in winter in cooling motor-car radiators, machine-gun barrels, etc.

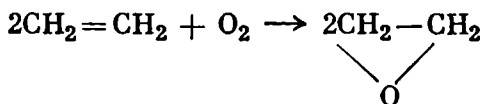
Ethylene glycol is also an ingredient of hydraulic brake liquids in artillery pieces and is used in the manufacture of plastics (pp. 436-39).

Ethylene glycol esters have many applications as solvents in the manufacture of lacquers.

Ethylene Oxide. By subjecting ethylene chlorohydrine to the action of an alcoholic solution of potassium hydroxide, Wurtz in 1858 prepared ethylene oxide:

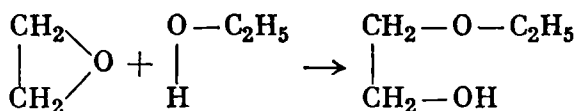


Ethylene oxide is prepared commercially by the oxidation of ethylene and other of the lower olefines by air at 150-350° in the gaseous phase over a catalyst (silver or gold):



Ethylene oxide is a gas, which condenses to a liquid boiling at 10.7°. Upon heating with water, ethylene oxide turns into ethylene glycol. It is an isomer of acetaldehyde.

Ethylene oxide is an extremely reactive compound with many uses in laboratory and industrial syntheses. For instance, upon heating in the presence of a small amount of sulphuric acid (catalyst), it adds alcohols, forming glycol monoethers:



Such monoethers, as well as glycol mixed ethers, are called *cellosolves* and serve as solvents in the manufacture of nitrocellulose lacquers.

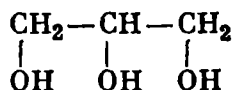
Compounds of considerable importance are formed by the addition of several molecules of ethylene oxide to aliphatic and aromatic alcohols. These addition products are used extensively as surface-active substances. They serve for the manufacture of *non-ionic detergents*, which preserve their detergent action even in sea-water.

Trihydroxy Alcohols, or Glycerols

The trihydroxy alcohols contain three hydroxyl groups. They are also called glycerols. The first representative of the group, called simply glycerol, or glycerine, is of quite exceptional importance.

69. Glycerol. The structure of glycerol $\text{C}_3\text{H}_8\text{O}_3$ is confirmed by the fact that it gives rise to three series of metal derivatives (glycerates) and that its three hydroxyls are halogen-replaceable. Its

molecule therefore contains three hydroxyl groups: $C_3H_5(OH)_3$. Since each carbon atom can hold only one hydroxyl, the structure of glycerol must correspond to the formula:



Glycerol is thus a derivative of propane, in which three hydrogen atoms have been replaced by three hydroxyls. In the Geneva nomenclature its name is propanetriol-1,2,3.

Glycerol was discovered in 1783 by K. Scheele, who found that the treatment of olive oil with lead oxide produces a specific sweet substance. He demonstrated that the same substance can be prepared from other fatty oils, as well as from solid fats.

Glycerol is made from fats (at candle and sometimes at soap factories) and from saccharoid substances by fermentation in the presence of sodium sulphite (p. 310). A method has been developed lately for preparing it synthetically, the raw material being propylene obtained from petroleum cracking gases.

Glycerol is a viscous syrupy liquid with a sweet taste (relative density 1.26). It boils at 290° , is miscible with water in all proportions, and is very hygroscopic.

To obtain crystalline glycerol, it is cooled to 0° and a glycerol crystal is introduced into it to initiate crystallization; its melting point is 17° .

Because it is hygroscopic, glycerol prevents objects with which it has been covered from drying. It is for this reason that it is used in cosmetics, in the tanning industry, and in the textile industry, where it serves to make fabrics soft and elastic. Considerable amounts of it are used in the tobacco industry, as well as to make antifreezes.

But the bulk of the glycerol manufactured is used in the production of nitroglycerine (p. 165) and glycerol-phthalic resin, which serves to make plastics known as *glyptals* (pp. 436-39). Glyptals find many applications in electrical engineering, especially in the manufacture of mica insulators, called *micanites*. Highly adhesive, heat resistant, non-fusible, and possessing relatively high dielectric properties, glyptals are in many cases indispensable in high-voltage electrical engineering. Large quantities of glycerol-phthalic resins are used to make the cement for electric bulb screw bases, as well as in lacquer manufacture.

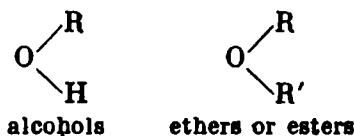
70. Polyhydroxy Alcohols. There are alcohols with an even greater number of hydroxyls in the molecule, e.g., the tetrahydroxy alcohol erythrite $C_4H_6(OH)_4$, which is known in the form of four stereois-

mers, and the various pentitols $C_5H_7(OH)_5$ and hexitols $C_6H_8(OH)_6$, which form numerous stereoisomers.

Some of them (D-sorbitol, D-mannitol, and dulcitol) are described in the chapter on carbohydrates.

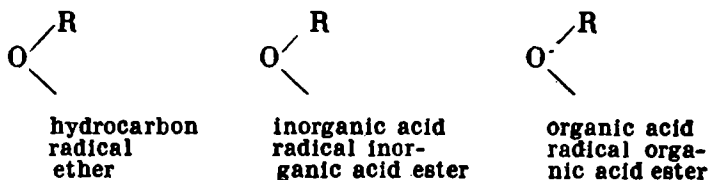
ETHERS AND ESTERS

By replacing the hydrogen atom of a hydroxyl in the alcohol molecule by a radical R' , we obtain ethers or esters:



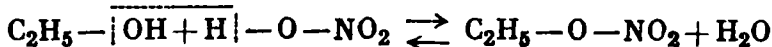
Depending on the nature of the R' radical (R is always a hydrocarbon radical), it is customary to distinguish three types of compounds:

- (1) *ethers* (R' is a hydrocarbon radical);
- (2) *esters of inorganic acids* (R' is an inorganic acid radical: NO_2 , NO , SO_3H , etc.);
- (3) *esters of organic acids* (R' is an organic acid radical):

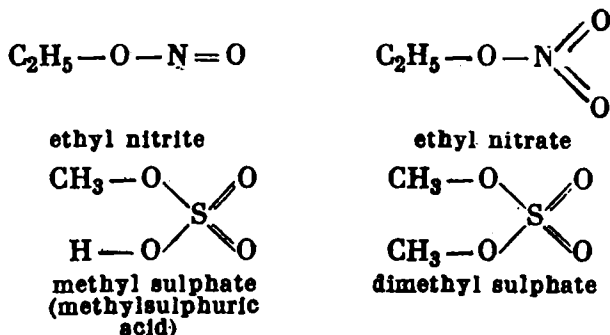


Esters of Inorganic Acids

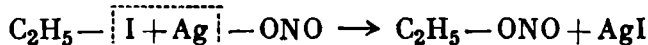
71. Preparation and Properties of Esters of Inorganic Acids. Alcohols can react with acids, the acid hydrogen being replaced by an alcohol radical:



The resulting substances are called esters. The following are examples of esters:



Esters can also be prepared by other methods, e.g., the action of salts on alkyl halides:

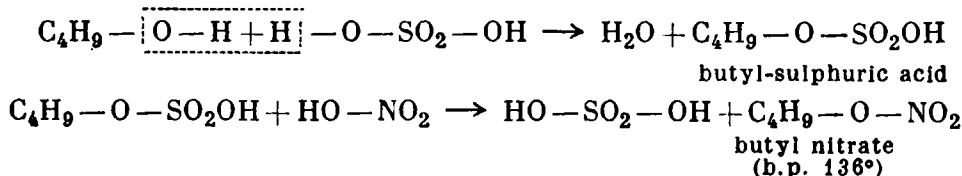


The reaction of ester formation (esterification) by the interaction of an alcohol with an acid is a balanced and reversible reaction.

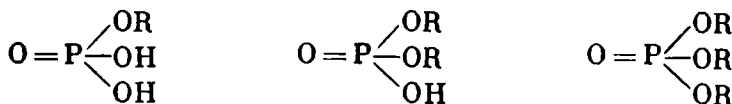
The dehydrating agent customarily used is concentrated sulphuric acid; the resulting ester is distilled off from the reaction mixture.

If the ester does not contain free acid or hydroxyl hydrogens, it is called a *neutral ester*; if, however, it does contain such hydrogen, it is called an *incomplete ester*; when the ester molecule contains a free acid hydrogen, it is called an *acid ester*.

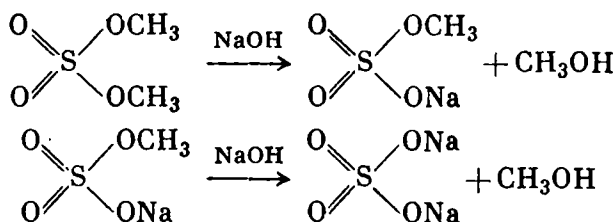
For instance, an alcohol reacts with concentrated sulphuric acid to form a non-volatile acid ester of sulphuric acid (an intermediate product), which upon treatment with nitric acid gives a neutral ester:



Similarly, phosphoric acid gives rise to three series of esters:

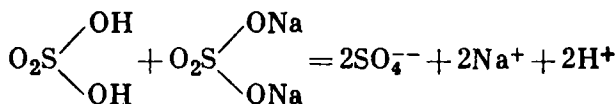


The neutral esters of inorganic acids corresponding to the first few members of the alcohol series are volatile liquids with a pleasant odour, which are immiscible with water. When esters are boiled with aqueous solutions of alkalis, they are broken up into an alcohol and salt:

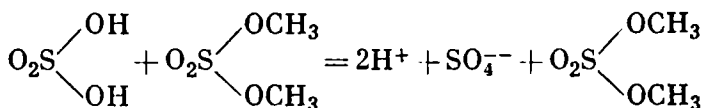


The structural formulas of esters are similar to those of salts. In properties, however, there is a pronounced difference between them. Salts are, as a rule, solid non-volatile substances, soluble in water and insoluble in organic solvents. Esters, on the other hand, are usually liquid and volatile, with a low solubility in water and high solubility in organic solvents. This difference is due to the

fact that salts are compounds of the ionic type. An aqueous solution of sodium hydrogen sulphate, for example, is completely identical to a mixture of sodium sulphate and sulphuric acid:

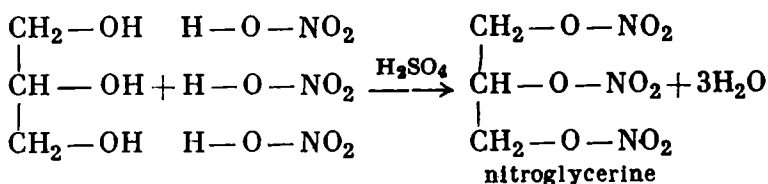


Esters, however, are homoeopolar (p. 62); the alkyl radicals do not form ions in solution. For example, the acid ester of sulphuric acid $\text{HOO}_2\text{SOCH}_3$ is a substance of entirely different properties than a mixture of sulphuric acid and dimethyl sulphate:



Dimethyl sulphate $(\text{CH}_3\text{O})_2\text{SO}_2$ or $(\text{CH}_3)_2\text{SO}_4$ is a liquid with a characteristic odour (b.p. 188° , relative density 1.35). It is often used in chemical syntheses for introducing the CH_3 group. Work with dimethyl sulphate calls for a number of precautions because its vapours are very poisonous.

72. Nitroglycerine. Nitroglycerine $\text{C}_3\text{H}_5(\text{ONO}_2)_3$, an ester of glycerol and nitric acid, is prepared by the action of a mixture of nitric and sulphuric acids on glycerol:

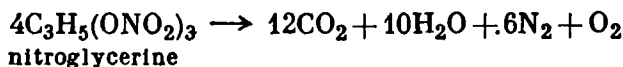


The sulphuric acid serves to bind the water resulting from the interaction of glycerol and nitric acid.

Nitroglycerine is a viscous oily liquid, which solidifies in the cold. It is a most powerful explosive. It explodes if struck, shaken, detonated by a mercury fulminate charge or as a result of spontaneous decomposition. Its vapours are highly toxic. Nitroglycerine is not used as an explosive in pure form, but serves to make nitroglycerine gunpowder and dynamites.

Dynamites are powdery, plastic, or gelatinous explosives containing nitroglycerine as the active base. They are prepared by impregnating various absorbents with nitroglycerine, i.e., substances with which they form a solid mass. The absorbents used are wood flour, nitrocellulose, diatomite, saltpetre, etc. Dynamites are more stable and safer to handle than nitroglycerine; they are far less sensitive to impact and shock, and they have many engineering applications.

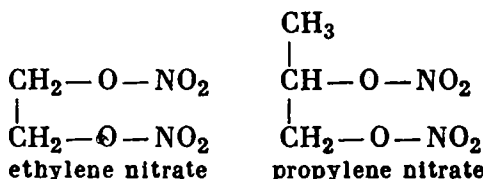
The instability of nitroglycerine is due to the structure of its molecule. Besides the carbon and hydrogen atoms, the nitroglycerine molecule contains enough oxygen atoms to burn all the carbon atoms to carbon dioxide and the hydrogen atoms to water. This is prevented by the nitrogen atoms in the molecule, which serve as something in the nature of a barrier separating the oxygen atoms from the carbon and hydrogen atoms and which seek to combine with one another to form stable molecules. The least cause (such as a slight shock) can produce a regrouping of the atoms, with the formation of carbon dioxide, water, oxygen, and nitrogen:



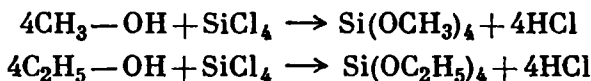
The reaction is attended by the evolution of an enormous amount of heat.

The regrouping instantly embraces the whole mass of nitroglycerine, and the resulting evolution of a large amount of gases produces an explosion of devastating power.

Along with nitroglycerine, *nitroglycols* have lately acquired great importance as explosives. These are esters of glycols and nitric acid:



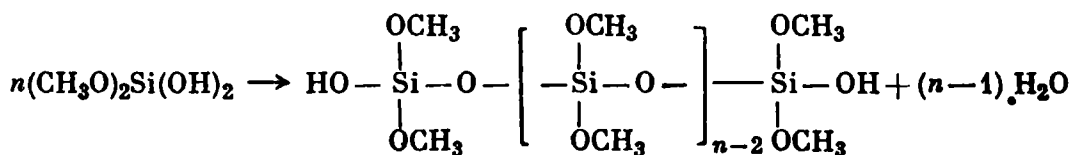
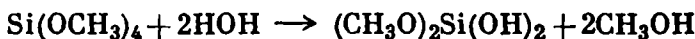
73. Esters of Orthosilicic Acid. The interaction of an alcohol and silicon tetrachloride produces an ester of orthosilicic acid:



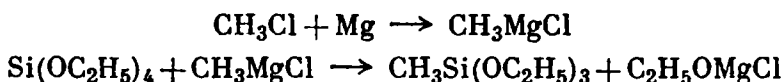
Esters of propyl, butyl, and isobutyl alcohols are prepared similarly.

Esters of orthosilicic acid have many applications.

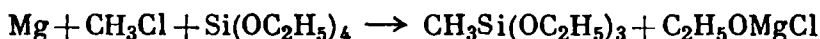
K. Andrianov has shown that the hydrolysis of the esters of orthosilicic acid is accompanied by polycondensation, which produces polymers of industrial value:



The same pattern of behaviour is followed by the esters of the alkylsilicic acids. These esters are produced industrially from alkyl chlorides and esters of orthosilicic acid by the Grignard reaction:



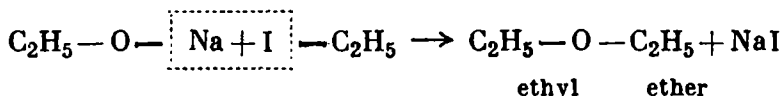
or by the direct action of the alkyl chloride and ester mixture on metallic magnesium:



Ethers

74. Structure and Preparation of Ethers. Ethers, exemplified by the well-known ethyl (sulphuric) ether $\text{C}_4\text{H}_{10}\text{O}$, are isomeric with alcohols. Ethyl ether, for instance, has the same composition as butyl alcohol; methyl ether $\text{C}_2\text{H}_6\text{O}$ is an isomer of ethyl alcohol.

The constitution of these substances becomes clear when we consider their preparation from alcoholates and alkyl halides (the *Williamson synthesis*):



From this synthesis it follows that the two hydrocarbon radicals in ethers are linked through an oxygen atom.

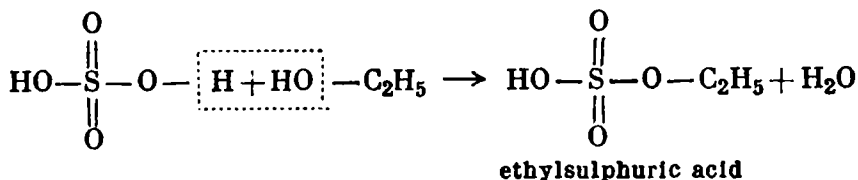
The name of the ether is determined by the names of the radicals:

$\text{CH}_3-\text{O}-\text{CH}_3$	methyl (dimethyl) ether
$\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$	ethyl (diethyl) ether
$\text{CH}_3-\text{O}-\text{C}_3\text{H}_7$	methyl propyl ether
$\text{C}_2\text{H}_5-\text{O}-\text{C}_3\text{H}_7$	ethyl propyl ether

If the two alkyl groups are different, the ether is said to be a *mixed ether*.

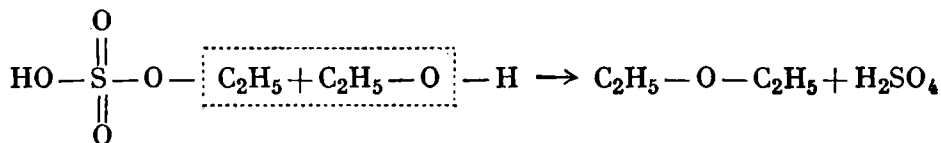
Some ethers can be prepared by heating the corresponding alcohol with concentrated sulphuric acid. Ethyl ether, which is industrially the most important of the ethers, may be prepared in this way.

The alcohol and the sulphuric acid at first form ethylsulphuric acid

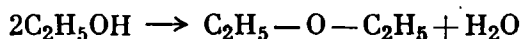


i.e., a product of the substitution of an ethyl group for one hydrogen atom in the molecule of sulphuric acid.

Ethylsulphuric acid then reacts with another alcohol molecule:

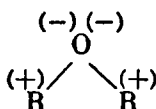


The over-all reaction is expressed by the equation:



Another method used extensively to prepare ethyl ether is the passage of ethyl alcohol vapours at 240-260° over aluminium oxide, which serves as a catalyst.

The molecules of even quite symmetric ethers have a dipole moment. As in the case of water, it is due to the fact that the bonds of the carbon atoms with the oxygen atom form a certain angle:



75. Properties of Ethers. The lowest representatives of the ethers boil at lower temperatures than the isomeric alcohols:

Alcohol	B.p., °C	Ether	B.p., °C
CH ₃ OH	65	(CH ₃) ₂ O	-23.6
C ₂ H ₅ OH	78	(C ₂ H ₅) ₂ O	35.6
C ₃ H ₇ OH	97	(C ₃ H ₇) ₂ O	90.7

The ethers likewise have a lower relative density than the corresponding alcohols. For example, the relative density of C₂H₅OH is 0.790, while that of (C₂H₅)₂O is 0.714.

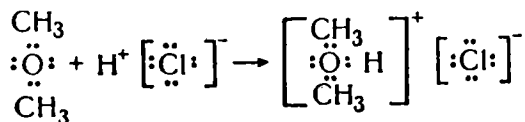
Methyl ether and ethyl methyl ether are at ordinary temperature gases, while the more complex ethers are highly volatile liquids; the ethers beginning with (C₁₇H₃₅)₂O are solids.

Ethers have a low reactivity: they undergo no change when heated with water, alkalis, or dilute acids. Unlike alcohols, they do not generate hydrogen when treated with metallic sodium.

The attitude of ethers to concentrated hydrochloric and hydrobromic acids is somewhat specific: they dissolve in these acids with the evolution of heat. It has been demonstrated that this is accompanied by the formation of unstable salt-like compounds known as *oxonium* compounds (by analogy to ammonium compounds). The electronic theory offers the following explanation for the formation of oxonium compounds.

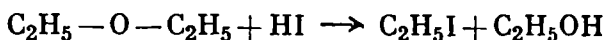
The oxygen atom of an ether has two pairs of free electrons; the positively charged hydrogen ion of hydrochloric acid, deprived of an electron, can avail itself of a free electron pair of the oxygen

to form an unstable positively charged oxonium ion:



When oxonium compounds are diluted with water, molecules of water displace the ether molecules, which leads to the destruction and decomposition of the oxonium compounds.

When ethers are saturated with hydrogen iodide, even at ordinary temperature, there is a rupture of the ether molecules as the site of the oxygen bond:



76. Ethyl Ether. Ethyl ether (C_2H_5)₂O is sometimes called simply ether or sulphuric* ether. It is a mobile colourless liquid, which boils at 35.6° and freezes at -117.6° (relative density 0.714). Its solubility in water is low: at 16° one litre of water dissolves about 100 ml of ether; 1 litre of ether dissolves approximately 30 ml of water. Ether is extremely volatile and highly inflammable. Its vapour is about two and a half times as heavy as air and forms explosive mixtures with it. When working with ether in the laboratory, it must always be borne in mind that its heavy vapour can spread far along the surface of a table or the floor and can catch fire from a nearby burner or electric heater. Ether is kept in thick-walled vessels with good stoppers, because even a slight rise in temperature considerably increases its vapour tension.

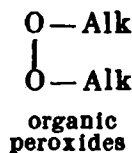
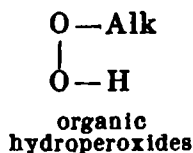
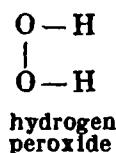
Ether is used as an anaesthetic. Large amounts of it are utilized in the production of smokeless gunpowder and collodion. An excellent solvent, it has many uses in the laboratory for the extraction and crystallization of organic substances. The industrial use of ether as a solvent is limited because of its high inflammability.

Anhydrous ether, known as "absolute" ether, is used as a solvent in many chemical reactions (the Wurtz reaction and organomagnesium syntheses). It is prepared from commercial ether, which is washed with water to remove the admixtures of alcohol, dried with fused calcium chloride, and distilled with metallic sodium shavings (or wire).

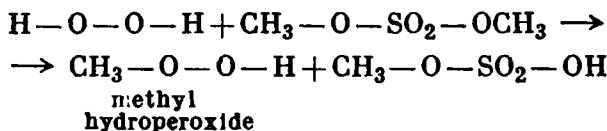
77. Organic Peroxide Compounds. As pointed out above (p. 126), alcohols can be viewed as derivatives of water. Similarly, organic

* The name "sulphuric" has survived from the time when the interaction of alcohol with sulphuric acid was the only method known for preparing ether.

peroxide compounds can be derived from hydrogen peroxide:

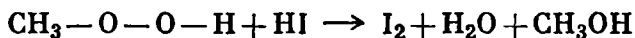


Methyl hydroperoxide is prepared by treating hydrogen peroxide with dimethyl sulphate:



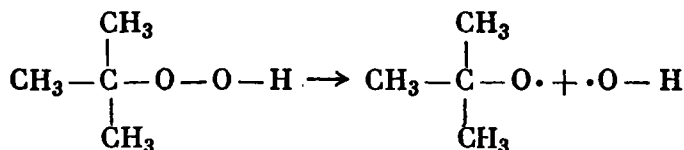
The methyl and ethyl hydroperoxides are compounds of low stability, which are highly explosive. Hydroperoxides containing secondary radicals are more stable, e.g., isopropyl hydroperoxide $(\text{CH}_3)_2\text{CH}-\text{O}-\text{O}-\text{H}$ and tertiary butyl hydroperoxide $(\text{CH}_3)_3\text{C}-\text{O}-\text{OH}$. These liquids can be distilled (they do not explode).

All the hydroperoxides react swiftly with hydrogen iodide, releasing iodine:



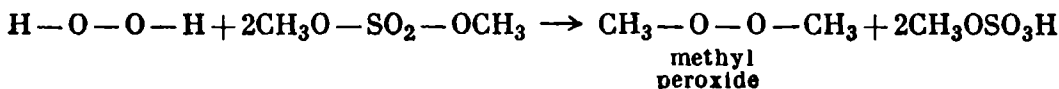
The qualitative detection and quantitative estimation of the hydroperoxides is based on this reaction.

When heated, the hydroperoxides form free radicals (p. 55):

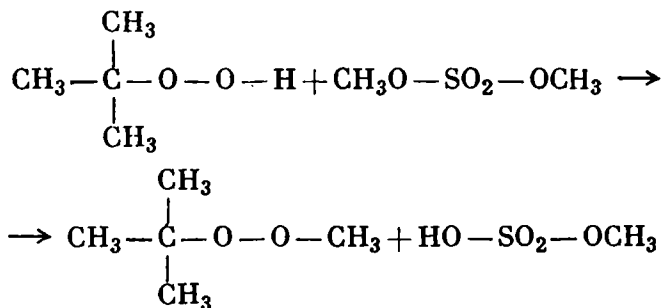


These free radicals induce chain reactions. For example, a 60% solution of tertiary butyl hydroperoxide in trimethylcarbinol initiates the polymerization of unsaturated compounds (p. 87).

Alkyl peroxides are prepared by the action of two molecules of dimethyl sulphate on hydrogen peroxide:

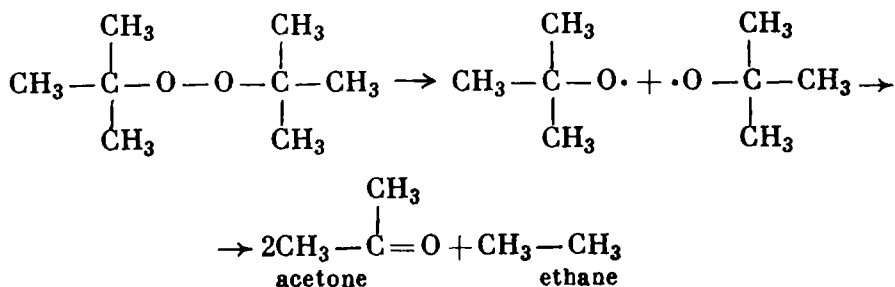


They can also be prepared by treating a dialkyl sulphate with the corresponding hydroperoxide:



Peroxides with different alkyls are prepared in this way.

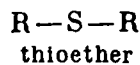
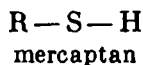
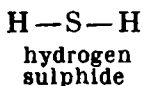
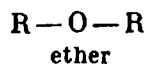
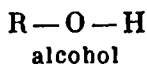
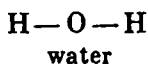
Methyl peroxide is a gas, which condenses into a liquid at 13.5°. Ethyl peroxide boils at 64°. The peroxides do not react as readily with HI as the hydroperoxides do. They are easily decomposed. The end products of the decomposition of tertiary butyl peroxide are acetone and ethane:



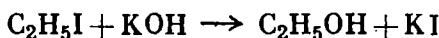
Like the hydroperoxides mentioned above, the peroxides are used as initiators of polymerization processes.

Mercaptans, Sulphonic Acids, Thioethers

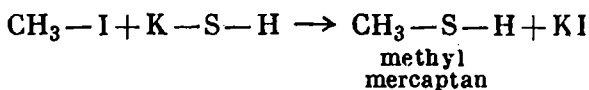
Alcohols and ethers may be viewed as derivatives of water, obtained by the substitution of hydrocarbon radicals for one or both hydrogen atoms in the water molecule. Similarly, mercaptans and thioethers may be regarded as derivatives of hydrogen sulphide, obtained by the substitution of hydrocarbon radicals for one or both hydrogen atoms in its molecule:



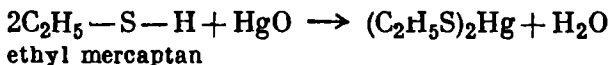
78. Mercaptans. We know that alcohols can be prepared by the action of alkalis on alkyl halides:



Mercaptans, also called *thioalcohols*, can be prepared similarly by the action of potassium hydrosulphide on alkyl halides:



Alcohols are derivatives of water, while mercaptans are derivatives of hydrogen sulphide. But whereas water is a neutral compound, hydrogen sulphide is a weak acid. Accordingly, alcohols exhibit neither acid nor basic properties, while mercaptans betray weak acid properties and form metal derivatives (*mercaptides*) when acted upon not only by alkalis, but also by oxides of heavy metals. Mercury compounds are especially characteristic of them:

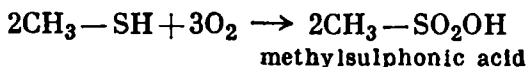


Hence the name mercaptan, which is a contraction of *mercurio corpus aptum*, i.e., a body with affinity for mercury.

Mercaptans have lower boiling points than corresponding alcohols. Methyl mercaptan, for instance, boils at 6°, whereas methyl

alcohol boils at 65°. Mercaptans are noted for a most disagreeable, extremely pungent odour.

79. Sulphonic Acids. The oxidation of the mercaptans by nitric acid converts them to sulphonic acids:

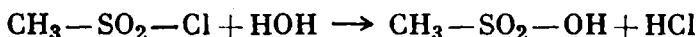


Sulphonic acids contain the sulpho-group SO_2OH , the sulphuric acid radical, with the sulphur atom linked to carbon. They are very strong acids and are readily soluble in water.

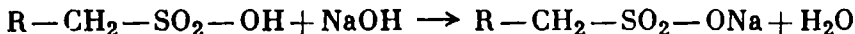
The action of phosphorus pentachloride on sulphonic acids produces *sulphonic acid chlorides*, or *sulphochlorides*:



The sulphochlorides are converted to sulphonic acids by the action of water:

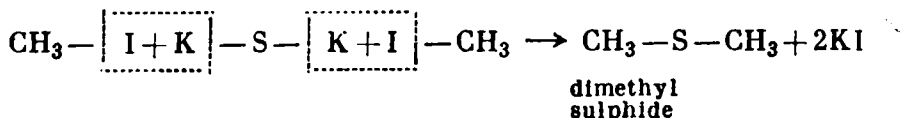


The sulphonic acids react with potassium hydroxide or soda to form salts; these are readily soluble in water and are called *sulphonates*:



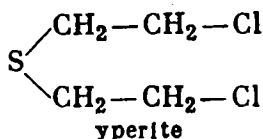
An economically very important method of preparing sulphonates is by so-called "photochemical sulphochlorination" (p. 57). The reaction of sulphochlorination produces a mixture of high-molecular alkylsulphonic acid chlorides. By neutralizing the mixture with soda, it is possible to obtain sulphonates, which are readily soluble in water and are used as detergents (p. 220).

80. Thioethers. The structure of the thioethers follows from their preparation by the interaction of alkyl halides and potassium sulphide:



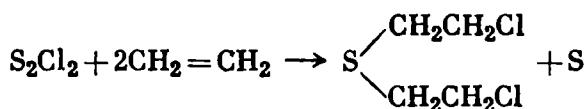
The lower thioethers are liquids insoluble in water. Like the salts of hydrogen sulphide, they are called *sulphides*.

One of the thioethers gained much notoriety in World War One. This was dichlorodiethyl sulphide



which came to be known as *yperite**, or *mustard gas* (unpurified yperite has a faint odour of mustard).

Yperite can be prepared by the action of ethylene on sulphur monochloride:



Yperite boils at 217°; purified yperite melts at 14°; unpurified, at a much lower temperature. Yperite is a chemical warfare agent, a vesicant: on contact with the skin it produces very persistent blisters. Its vapours affect the mucous membranes, respiratory tract, and skin of man and animals.

Yperite is considered one of the persistent war gases.

Individual protection is afforded by a gas mask and protective clothing. Neutralization is effected by bleaching powder, which simultaneously chlorinates and oxidizes yperite, turning it into non-toxic substances

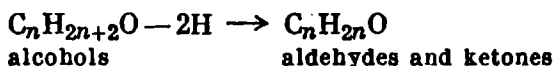
* Yperite was first prepared in 1886 by N. Zelinsky.

Aldehydes and Ketones (Oxo Compounds)

81. Structure, Isomerism, and Nomenclature of Oxo Compounds. The class of aldehydes and ketones consists of compounds whose molecules contain the carbonyl (or oxo) group $>C=O$:



As has been stated above (p. 137), aldehydes and ketones result from the oxidation of corresponding primary and secondary alcohols, provided oxidation does not affect the carbon chain. The alcohol molecule in this cases gives up two hydrogen atoms. The general formula for the aldehyde and ketone homologous series is thus the same:



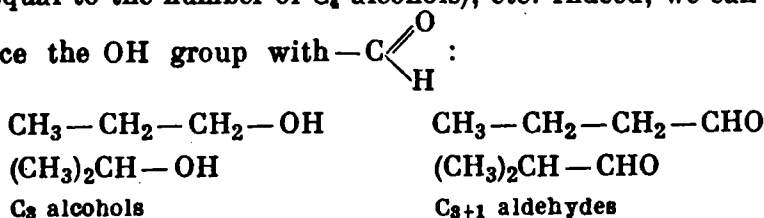
The number of isomeric aldehydes will evidently correspond to the number of primary alcohols (ketones, to the number of secondary alcohols) with as many carbon atoms. Tertiary alcohols cannot be turned into carbonyl compounds without a break-up of the carbon skeleton.

The following methods make it possible to calculate the number of possible isomers for aldehydes and ketones.

Let us assume that we know all the isomers of the alcohols up to C_6 :

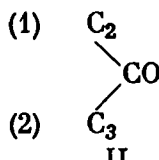
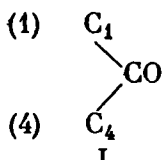
C_1	1	C_4	4
C_2	1	C_5	8
C_3	2	C_6	17

In that case it is easy to demonstrate that the number of aldehydes (or the number of primary alcohols, which amounts to the same thing here) for C_4 will equal the number of all the alcohols for C_3 ; similarly, the number of aldehydes for C_5 will be 4 (equal to the number of C_4 alcohols), etc. Indeed, we can always mentally replace the OH group with $-\text{C}(=\text{O})\text{H}$:



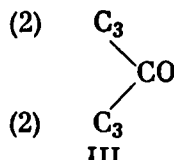
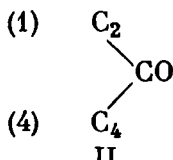
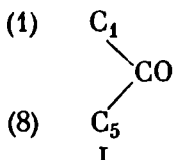
The number of ketones is calculated somewhat differently. Let us take as an example the calculation of the number of $C_6H_{12}O$ ketones.

The following types are possible:



Evidently system I has 4 isomers (1×4), while system II has 2 isomers (1×2). This makes a total of 6.

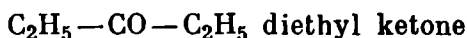
If n is an odd number, the calculation is slightly more complicated. For C_7 , for example, we have



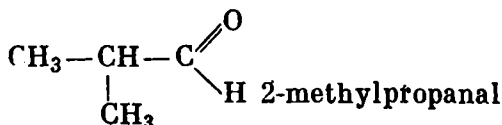
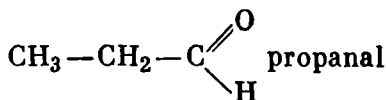
System I allows of 8 isomers; system II, of 4. For system III, however, the number of isomers will not be $4(2 \times 2)$, but one less, because of the recurrence of identical isomers: norm.-norm.; iso-iso; norm.-iso (and again iso-norm.). Consequently, the total number of C_7 ketones is:

$$8 + 4 + 3 = 15$$

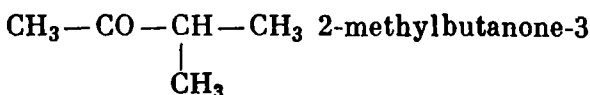
The names of the aldehydes were originally derived from the names of the acids formed by their oxidation: formaldehyde (formic aldehyde), acetaldehyde (acetic aldehyde), propionaldehyde, butyraldehyde, etc. The names of the ketones are usually based on the names of the radicals linked to the carbonyl group, e.g.:



The Geneva system denotes the presence of the aldehyde group by the suffix *al*:



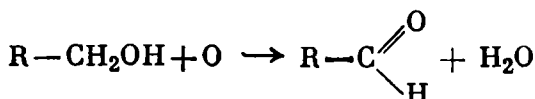
The presence of the ketone group is denoted by the ending *one*:



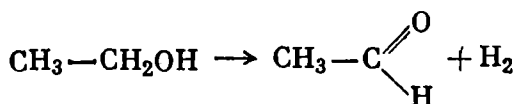
As far as properties are concerned, the aldehydes and ketones have much in common. It will therefore be convenient to give a parallel description of these classes of substances.

82. Preparation and Certain Properties of Aldehydes. Aldehydes can be prepared by several methods. Three of them are described below.

1. Oxidation of primary alcohols:



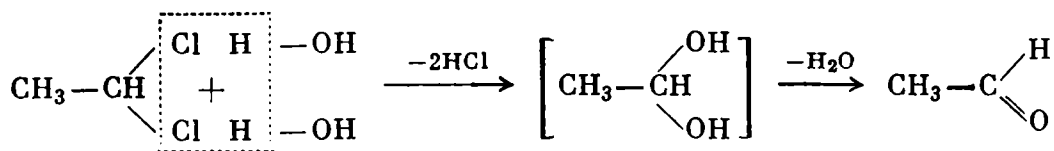
This method of preparing aldehydes reveals the origin of their name. The name "aldehyde" is a contraction of the Latin words *alcohol dehydrogenatus*, i.e., alcohol deprived of hydrogen. It is noteworthy that an alcohol can also be converted to an aldehyde in the absence of oxygen, if the alcohol is shaken with finely divided palladium, which is capable of absorbing hydrogen:



Hydrogen can also be eliminated by leading the alcohol vapour at a high temperature (300°) over a copper or silver gauze in a refractory tube. The reaction of hydrogen elimination is called *dehydrogenation*.

2. Dry distillation of a mixture of calcium and barium salts of carboxylic acids (p. 212).

3. The heating with water of dihalogen derivatives in which both halogen atoms are attached to the same carbon atom at the end of the chain:



At first substances with two hydroxyls attached to the same carbon atom are formed; these may be regarded as aldehyde hydrates. On giving up water, they become aldehydes. In aqueous solutions aldehydes nearly always exist partly in the form of such hydrates.

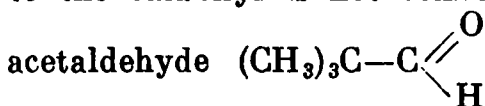
The simplest of the aldehydes is formaldehyde, a gas with a pungent unpleasant odour. The intermediate homologues are liquids, also with pungent unpleasant odours. The higher aldehydes (C_{10} and higher), when diluted, have flower odours; many of them occur in the essential oils of flowers. For example, nonyl aldehyde $\text{C}_9\text{H}_{17}\text{CHO}$ occurs in rose oil. Some of the substances in this class are used in the perfume industry.

TABLE 5. Physical Properties of the Simplest Aldehydes

Aldehyde	Formula	Relative density d_4^{20}	B.p., °C
Formaldehyde	H—CHO	0.815 (at -20°)	-19.2
Acetaldehyde	CH ₃ —CHO	0.780	20.8
Propionaldehyde	CH ₃ CH ₂ —CHO	0.807	49.1
Normal butyraldehyde	CH ₃ CH ₂ CH ₂ —CHO	0.817	75
Isobutyraldehyde	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} - \text{CHO} \\ \diagdown \\ \text{CH}_3 \end{array}$	0.794	64
Valeraldehyde	CH ₃ —CH ₂ CH ₂ CH ₂ —CHO	0.819 (at 11°)	102

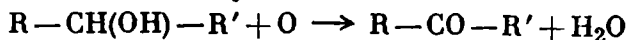
It is characteristic of aldehydes that when they are added to fuchsin-sulphurous acid*, its colour turns to crimson or violet.

Alkalis resinify aldehydes, turning them into reddish-yellow substances known as aldehyde resin. Formaldehyde is not resinified by alkalis. Nor are other aldehydes in which the carbon atom next to the carbonyl is not connected with hydrogen, e.g., trimethyl-



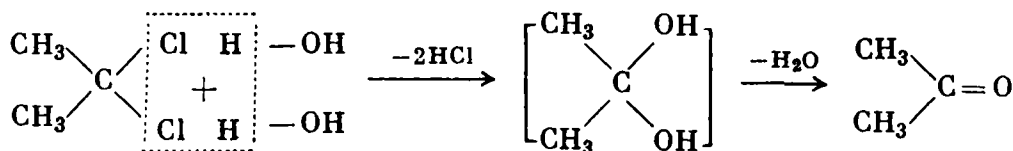
83. Preparation and Certain Properties of Ketones. The methods for the preparation of ketones are analogous to the methods for the preparation of aldehydes.

1. Oxidation of secondary alcohols:



2. Dry distillation of calcium and barium salts of carboxylic acids (p. 212).

3. The heating with water of dihalogen derivatives in which both halogen atoms are attached to the same carbon atom, which is not at the end of the chain:



* Fuchsin-sulphurous acid is prepared by passing sulphur dioxide into a magenta-coloured fuchsin solution until it is completely discoloured. Alternatively, it can be prepared by shaking a highly diluted aqueous solution of fuchsin with a few drops of sodium hydrogen sulphite solution.

The lower and middle members of the ketone homologous series are liquids. Some of them have pleasant odours, but some have an unpleasant rancid odour. Unlike aldehydes, ketones do not produce a coloration of fuchsin-sulphurous acid.

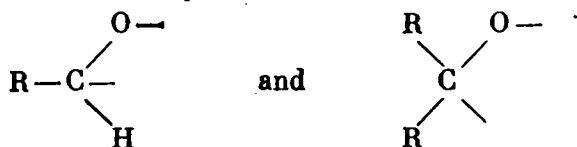
TABLE 6. Physical Properties of the Simplest Ketones

Ketone	Formula	Relative density d_4^{20}	B.p., °C
Dimethyl ketone (acetone)	$\text{CH}_3-\text{CO}-\text{CH}_3$	0.7980	56.1
Ethyl methyl ketone . .	$\text{CH}_3-\text{CO}-\text{C}_2\text{H}_5$	0.8058	79.6
Diethyl ketone	$\text{C}_2\text{H}_5-\text{CO}-\text{C}_2\text{H}_5$	0.8138	101.8
Methyl propyl ketone .	$\text{CH}_3-\text{CO}-\text{C}_3\text{H}_7$	0.8089	100.8
Methyl butyl ketone . .	$\text{CH}_3-\text{CO}-\text{C}_4\text{H}_9$	0.830	127.7
Dipropyl ketone	$\text{C}_3\text{H}_7-\text{CO}-\text{C}_3\text{H}_7$	0.818	144
Diisobutyl ketone . . .	$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\ \qquad \qquad \quad \\ \text{CH}-\text{CH}_2-\text{CO}-\text{CH}_2-\text{CH} \\ \qquad \qquad \quad \\ \text{CH}_3 \qquad \qquad \text{CH}_3 \end{array}$	0.895	166

REACTIONS OF ALDEHYDES AND KETONES

Aldehydes and ketones—the former, especially—are highly reactive compounds. They are capable of addition, substitution, and oxidation reactions.

84. Addition Reactions. Aldehydes and ketones enter into addition reactions thanks to the fact that the double bond between the oxygen and the carbon in the carbonyl group readily becomes a single bond; this gives the carbon and oxygen atoms each a free valency, which are saturated by the valency units of other atoms:

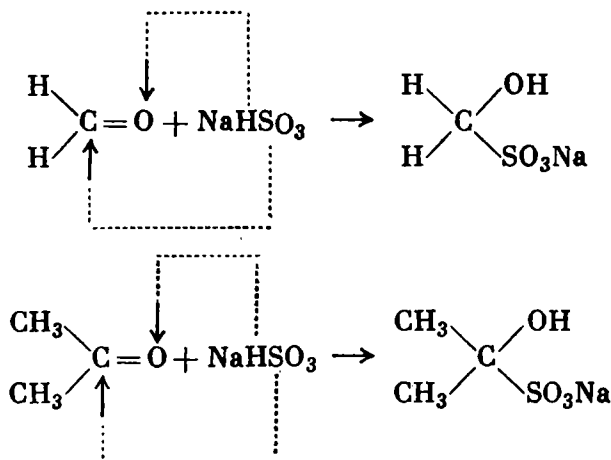


1. Aldehydes and those ketones that contain a methyl group linked to the carbonyl, i.e., the $\text{CH}_3-\text{C}-$ group, are capable



of adding sodium hydrogen sulphite (sodium bisulphite). The resulting compounds are called *bisulphite compounds*.

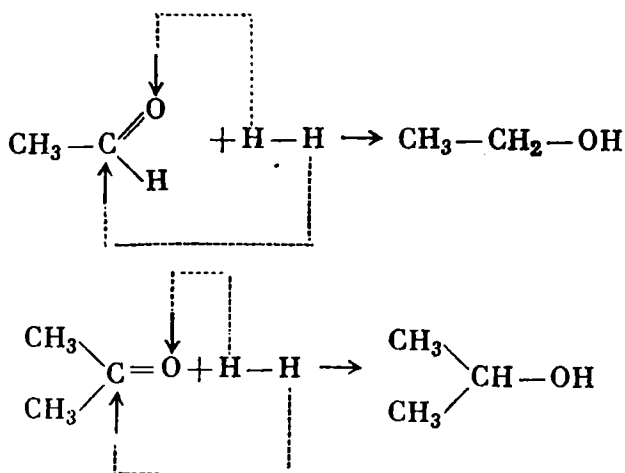
In these substances sulphur is directly linked to carbon:



The reaction is conducted by shaking the aldehyde or ketone with as concentrated a solution of NaHSO_3 as possible.

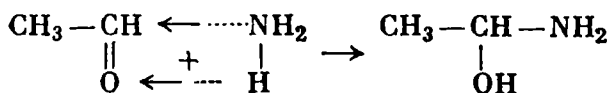
Bisulphite compounds are crystalline substances, which break up upon heating with a soda solution or dilute acids to form aldehydes and ketones. They serve to isolate aldehydes and ketones from mixtures with other substances and to obtain them in pure form.

2. Aldehydes and ketones are capable of adding hydrogen; the aldehydes in this case form primary alcohols, the ketones, secondary:



The reaction can be effected by passing a mixture of hydrogen and the aldehyde or ketone vapour over finely divided nickel or by using hydrogen in the nascent state.

3. With ammonia aldehydes form crystalline compounds called aldehyde ammonias:

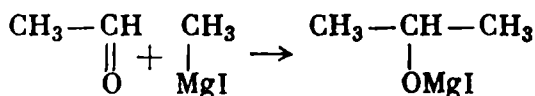


Even a freshly prepared aldehyde ammonia is, however, a polymerization product; its molecular weight is three times the figure it should be according to the above formula, which reflects only the first stage of the reaction.

The action of dilute acids breaks up the aldehyde ammonias into the initial aldehydes and ammonium salts.

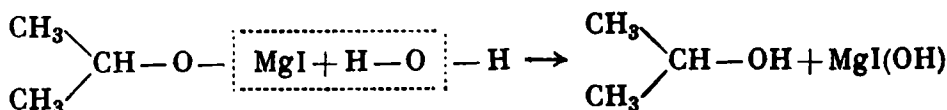
Ketones with ammonia give complex products.

4. Aldehydes and ketones are capable of adding organomagnesium compounds. For example, when acetaldehyde is added to an ethereal solution of methylmagnesium iodide, a bulky precipitate of the addition product is formed:



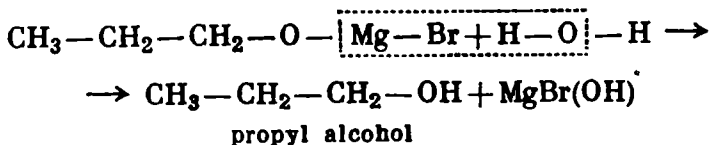
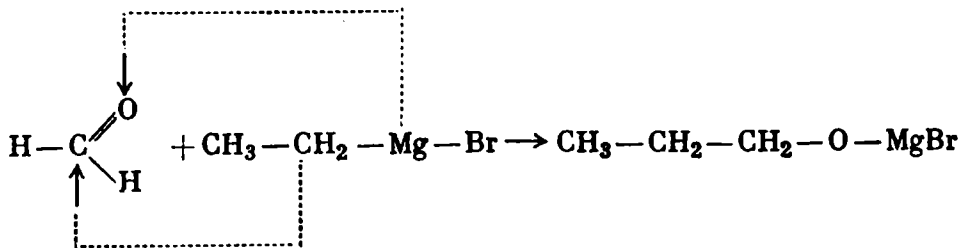
As is evident from the equation, the organomagnesium compound radical is added to the carbon atom, while the rest of the molecule is added to the oxygen atom. The reaction is conducted in a solution of thoroughly dehydrated ("absolute") ether in an apparatus with a reflux condenser. The addition product is an alcoholate.

Its decomposition by an aqueous solution of an acid produces isopropyl alcohol:

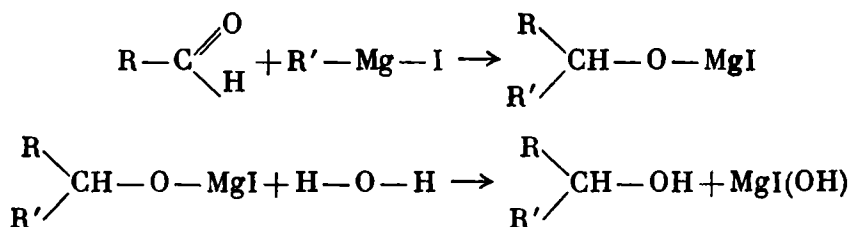


The reaction makes it possible, proceeding from an aldehyde, to obtain a secondary alcohol with a greater number of carbon atoms in the molecule.

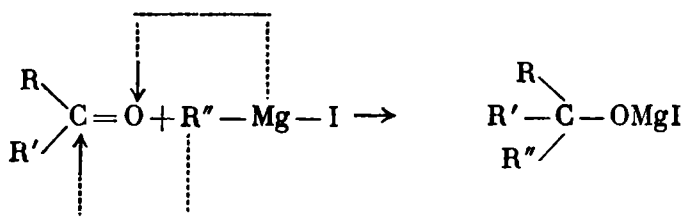
In the case of formaldehyde the reaction yields a primary alcohol:



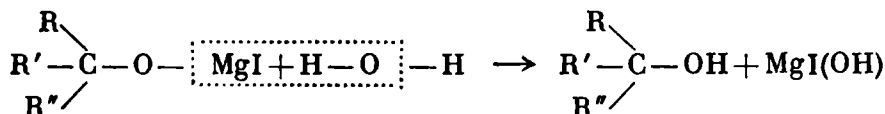
In general form the reaction for aldehydes can be written as follows (with R a radical or, for formaldehyde, hydrogen):



The reactions with ketones proceed quite analogously:

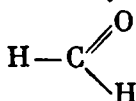


Decomposed by water, the addition products yield tertiary alcohols:



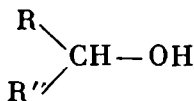
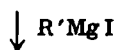
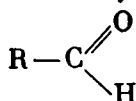
By means of organomagnesium compounds it is thus possible to prepare primary, secondary, and tertiary alcohols with a greater number of carbon atoms in the molecule than the initial aldehyde or ketone had:

formaldehyde



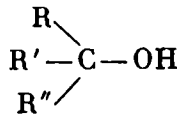
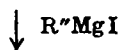
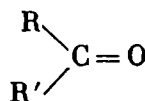
primary alcohol

other aldehydes



secondary alcohols

ketones



tertiary alcohols

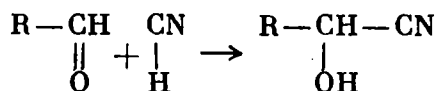
The reaction of alcohol preparation by means of organometallic compounds was discovered by A. Zaitsev*. With his co-workers,

* Alexander Zaitsev (1841-1910) was one of Butlerov's foremost pupils. He was born at Kazan, where he received his education and worked. From 1871 to the end of his life he held the chair in organic chemistry at the University of Kazan.

he in 1874 and the following years synthesized a considerable number of various alcohols by means of organozinc compounds.

At present these syntheses are conducted by means of organomagnesium compounds.

5. Aldehydes and ketones add hydrogen cyanide to form hydroxynitriles:

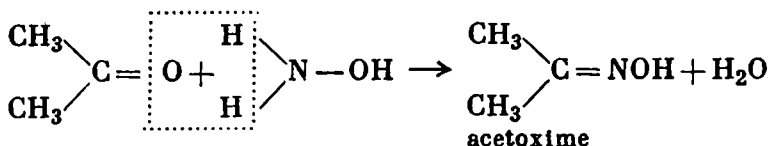
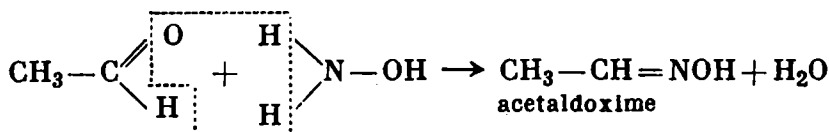


Hydroxynitriles can easily be converted to hydroxy acids (p. 261 fol.) and amino acids (p. 340 fol.).

6. Aldehydes are very easily polymerized, i.e., the molecules of the same aldehyde combine to form bigger molecules. Polymerization can give: 1) substances whose molecules can be depolymerized to molecules of the initial aldehyde, and 2) substances that cannot be depolymerized in this way (pp. 189-90). Ketones undergo polymerization less readily, the products always being of the second type.

85. Substitution Reactions. We shall confine ourselves to those substitution reactions that result in the replacement of an oxygen atom by a carbonyl group.

1. With hydroxylamine $\text{NH}_2\text{—OH}$ aldehydes and ketones give *oximes*:



The work of Zaitsev and his school was primarily aimed at developing Butlerov's ideas and building up experimental confirmation of the theory of chemical structure.

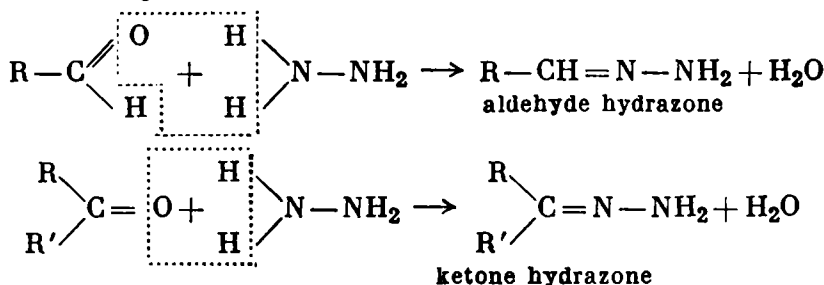
Zaitsev found a means of converting acid chlorides into corresponding alcohols and prepared *n*-butyl alcohol, the fourth and last of the butanol isomers.

Important work was also done by Zaitsev in studying the detachment of hydrogen halides from alkyl halides with the formation of olefines.

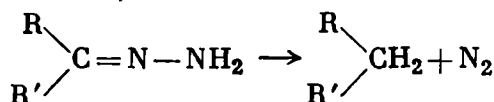
Zaitsev continued Butlerov's syntheses involving organozinc compounds and found the simple and accessible method of preparing secondary and tertiary saturated and unsaturated alcohols by the interaction of alkylzinc iodides and aldehydes or ketones.

Zaitsev founded a big school of talented pupils, many of whom subsequently held chairs in chemistry at Russian universities.

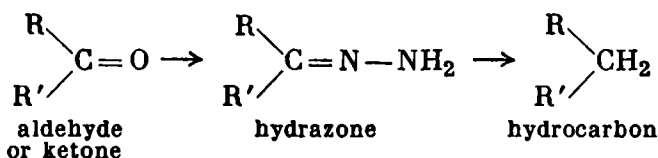
2. The action of hydrazine $\text{NH}_2\text{—NH}_2$ upon aldehydes and ketones produces *hydrazones*:



Solid alkalis or alcoholates decompose hydrazones; this is accompanied by the evolution of free nitrogen and the formation of hydrocarbons (*Kizhner reaction*):

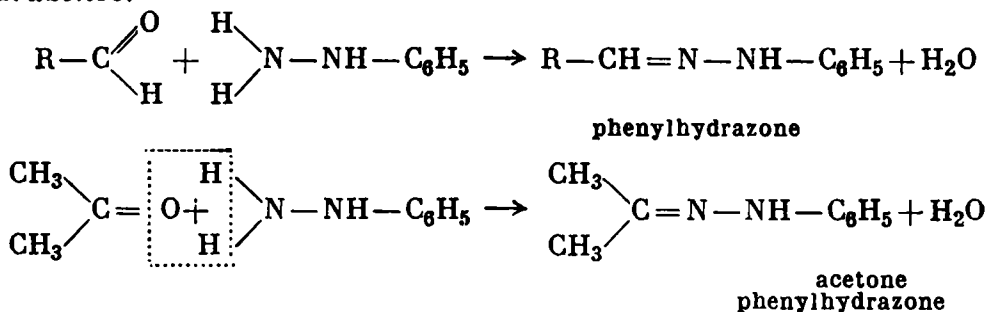


In this way hydrocarbons can be obtained from aldehydes or ketones:



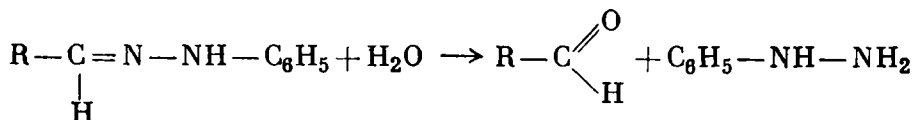
This reaction was discovered in 1910 by the Russian chemist N. Kizhner, who decomposed hydrazones by heating them in a flask with a small amount of potassium hydroxide (the reaction proceeds much better in the presence of bits of platinized clay). A year and a half after the publication of Kizhner's first papers about the reaction he had discovered the German scientist Wolff described the same reaction. Wolff's method differs only in that the reaction of hydrazone decomposition is conducted in a sealed tube.

3. Aldehydes interact with phenylhydrazine* to form *phenylhydrazones*:



* Phenylhydrazine is a derivative of hydrazine $\text{NH}_2\text{—NH}_2$, in which one atom of hydrogen has been replaced by the phenyl radical C_6H_5 . It melts at 20° and is practically insoluble in water, but forms soluble salts with hydrochloric acid.

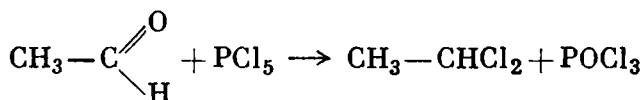
The reverse reaction takes place when phenylhydrazones are subjected to the action of acid solutions; in this case they add water and decompose to phenylhydrazine and an aldehyde or ketone:



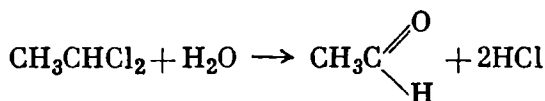
The hydrolysis of oximes proceeds similarly.

Oximes and phenylhydrazones are mostly crystalline substances with characteristic melting points. The reaction of their formation is used for the identification of this or that aldehyde or ketone, as well as to isolate aldehydes and ketones from mixtures with substances of other classes.

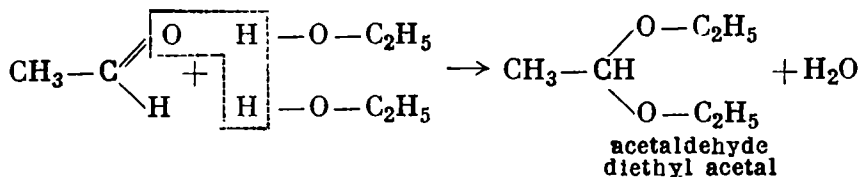
4. The action of phosphorus pentachloride causes an atom of oxygen in the aldehyde or ketone molecule to be replaced by two chlorine atoms:



This produces halogen derivatives of hydrocarbons with two halogen atoms attached to the same carbon atom. Such a dihalogen derivative reacts with water to give the initial aldehyde or ketone:



5. With alcohols, aldehydes condense to form *acetals*:



Acetals are prepared by heating an alcohol and aldehyde mixture with anhydrous copper sulphate or by boiling the aldehyde with an alcoholic solution of hydrogen chloride.

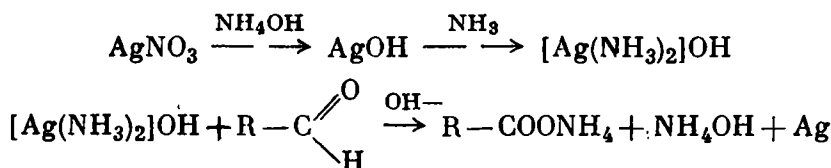
Acetals can be regarded as ethers of aldehyde hydrates. They are colourless liquids with a pleasant odour. An aqueous solution of an acid quickly decomposes an acetal into an aldehyde and an alcohol. Analogous compounds of ketones are known, but are prepared differently.

86. Oxidation of Aldehydes and Ketones. *Aldehydes* undergo oxidation readily. They can even be oxidized by the oxygen of the air and such weak oxidizing agents as an ammoniacal solution of silver oxide.

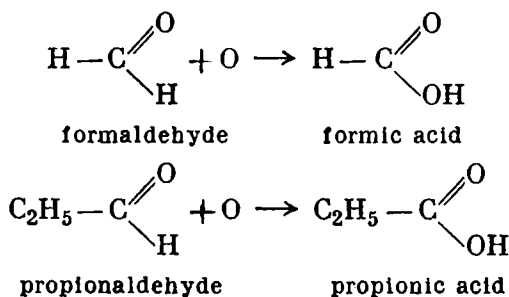
The reaction of aldehydes with ammoniacal silver oxide is known as the "silver mirror reaction" and is used to detect aldehydes.

The reaction is usually performed in the following manner. One-two ml of a 5% solution of silver nitrate are poured into a thoroughly washed test-tube, and a weak solution of ammonia is added by drops until the initially formed precipitate is dissolved. A drop of an aldehyde is then introduced, the contents of the test-tube are stirred, the test-tube is placed in hot water (60-70°) and left there for a few minutes. The reduced metallic silver is partly thrown down as a black precipitate and partly deposited on the walls of the test-tube in the form of a shiny mirror.

The reactions that take place can be expressed by the following equations:



Oxidation causes aldehydes to add oxygen; the substances formed are called *carboxylic acids*:



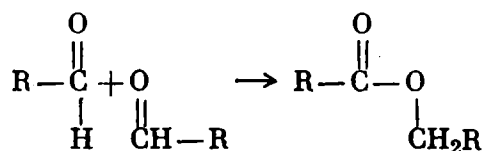
It is evident from the above equations that when aldehydes are oxidized, the oxygen atom becomes attached to the carbon atom that has an oxygen atom already.

Carboxylic acids are characterized by the group $-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{OH} \end{array}$ or $-\text{COOH}$,

which is called the *carboxyl*.

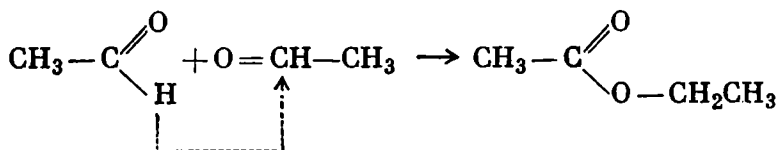
Tishchenko Reaction. The notable readiness of aldehydes to undergo oxidation or reduction is borne out most strikingly by the Tishchenko reaction (1906). If a small amount of some aluminium alkoxide—say, aluminium ethoxide $\text{Al}(\text{OC}_2\text{H}_5)_3$ —is added to some aldehyde, a vigorous reaction takes place: the double bond between the carbon and the oxygen is ruptured and the hydrogen of the aldehyde group of one molecule is added to the carbon of another, while the remaining part of the molecule is joined to the oxygen. An ester

is thus formed:



Hydrolysis of the ester yields an acid and alcohol. It might therefore be said that in the Tishchenko reaction one molecule of the aldehyde is oxidized at the expense of the reduction of another.

Consider the case of acetaldehyde. The Tishchenko reaction turns it into ethyl acetate:



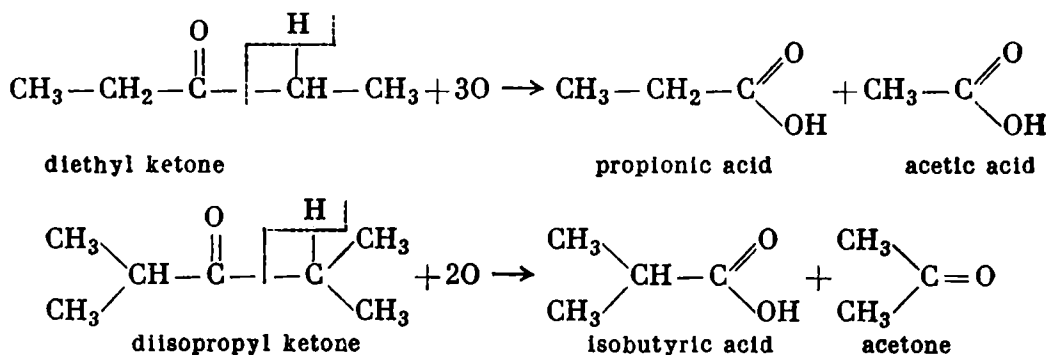
Let us now arrange in the form of a table the formulas of hydrocarbons, alcohols, aldehydes, acids with the same number of carbon atoms in the molecule:

CH_4	CH_3-OH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C} \\ \\ \text{OH} \end{array}$
methane	methyl alcohol	formaldehyde	formic acid
C_2H_6	$\text{C}_2\text{H}_5-\text{OH}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C} \\ \\ \text{OH} \end{array}$
ethane	ethyl alcohol	acetaldehyde	acetic acid
C_3H_8	$\text{C}_3\text{H}_7-\text{OH}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5-\text{C} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5-\text{C} \\ \\ \text{OH} \end{array}$
propane	propyl alcohol	propionaldehyde	propionic acid
C_4H_{10}	$\text{C}_4\text{H}_9-\text{OH}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_3\text{H}_7-\text{C} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_3\text{H}_7-\text{C} \\ \\ \text{OH} \end{array}$
butane	butyl alcohol	butyraldehyde	butyric acid
C_5H_{12}	$\text{C}_5\text{H}_{11}-\text{OH}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_4\text{H}_9-\text{C} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_4\text{H}_9-\text{C} \\ \\ \text{OH} \end{array}$
pentane	amyl alcohol	valeraldehyde	valeric acid

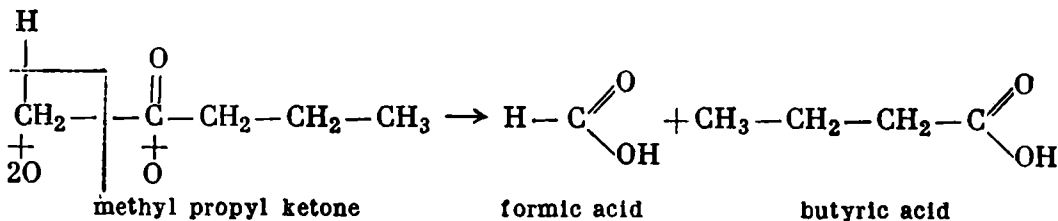
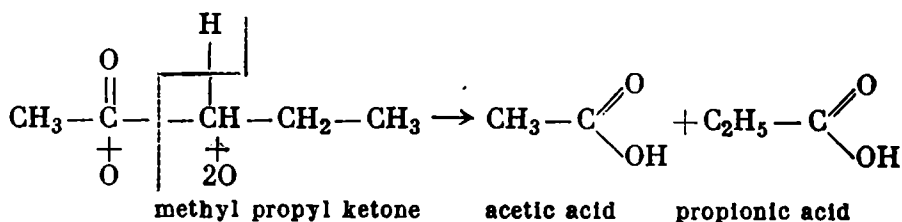
The compounds in each vertical column are members of the same homologous series. The substances in each horizontal line are derivatives of the same hydrocarbon; they can be derived one from the other by simple chemical reactions. "If a series is incomplete, we not

only know the composition of the missing members and their essential properties, but can also find ways of preparing them, should we want to supplement the series" (Schorlemmer).

Oxidation of Ketones. Ketones cannot be oxidized either by the oxygen of the air or by weak oxidizing agents; nor do they reduce an ammoniacal solution of silver oxide. The oxidation of ketones is effected by stronger oxidizing agents such as potassium permanganate; moreover, their oxidation proceeds differently than that of aldehydes. Upon oxidation, a ketone molecule breaks up, giving rise either to two molecules of an acid or to a molecule of an acid and a molecule of a ketone less complex than the initial one. The carbon atom chain breaks at the carbonyl carbon:



If the ketone molecule contains two different radicals, oxidation can cause the molecule to split up in two different ways:

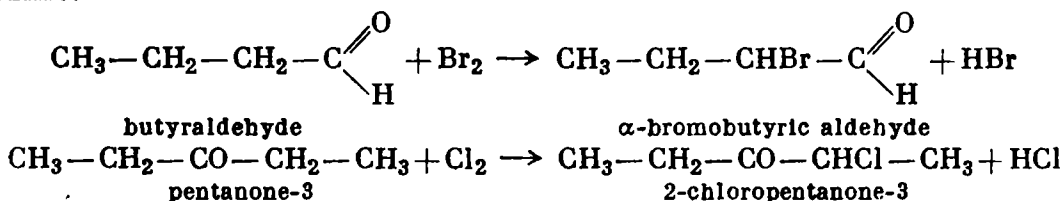


By oxidizing a ketone and identifying the acids formed, we are thus able to determine the structure of the ketone.

The rules for splitting ketones by oxidation were formulated by A. Popov.

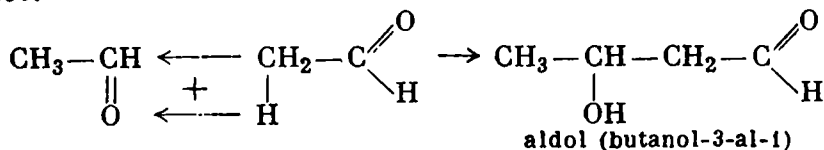
87. Reactions Involving the H-Atom on the C-Atom Alpha to the Carbonyl. The carbonyl group in aldehydes and ketones exerts a very strong influence on the hydrogen atoms attached to a carbon atom adjacent to it (and said to be in α -position).

These atoms are easily replaced by the action of chlorine or bromine:



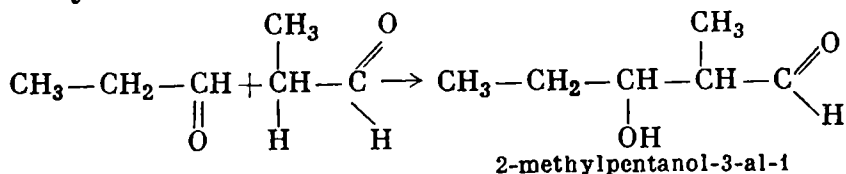
The halogen atoms close to the carbonyl are highly reactive. The α -halogenated aldehydes and ketones are strong lachrymators (from the Latin *lacrima*, meaning tear), this being due to the fact that their vapours irritate the mucous membranes of the nose and the eyes.

The condensation reactions of the ketones and, especially, of the aldehydes under the influence of alkaline solutions and certain other reagents are highly important. For example, the action of weak alkaline solutions of zinc chloride upon cold acetaldehyde turns it into *aldol*:

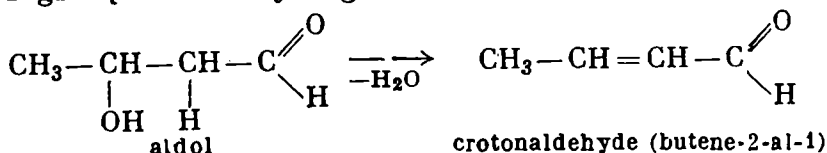


The reaction product, a liquid miscible with water, can be distilled without decomposition only at a reduced pressure. As may be seen from the formula, its molecule contains both the aldehyde group and the alcohol group (ald-ol).

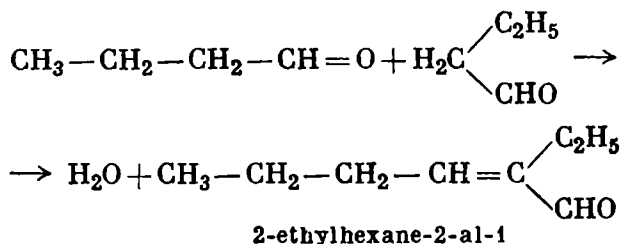
Similar aldols are obtained from the homologues of acetaldehyde. The reaction is known as the *aldol condensation*. It is made possible by the mobile α -hydrogen atom. In the case of propionaldehyde the reaction may be written as follows:



The aldols are rather unstable compounds; they readily lose the hydroxyl group and α -hydrogen, which form water:



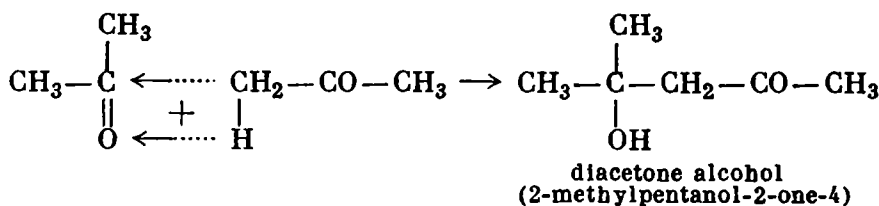
Aldehyde condensation with the elimination of water is called *crotonic*. The homologues of acetaldehyde with a free $>\text{CH}_2$ methylene group alpha to the carbonyl likewise readily undergo this type of condensation. For butyraldehyde, for instance, the reaction is:



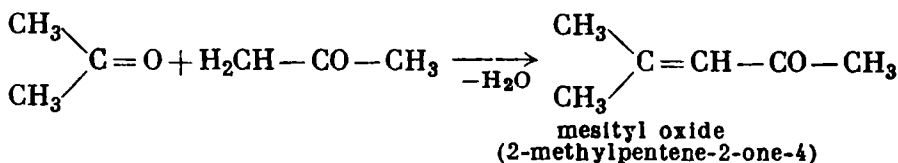
The action of strong alkalis upon aldehydes causes the process of condensation to proceed very vigorously; it results in the formation of resinous products, a mixture of high-molecular compounds. The reason for this is quite understandable. In the aldol formation, as in the crotonaldehyde formation, the aldehyde groups are preserved, and they can then enter into aldol and croton condensation reactions with one another and with molecules of the initial aldehydes.

Condensation reactions are usually defined as reactions that result in a lengthening of the carbon chain. The molecules in this case may condense without the elimination of simple molecules (as in the formation of aldols) or with their elimination (as in the crotonic condensation).

The most active ketones are, like aldehydes, capable of undergoing both the aldol and the croton condensation. Acetone, for example, when subjected to the action of barium hydroxide, undergoes an aldol condensation, yielding so-called diacetone alcohol:



The action of a strong alkali produces a crotonic condensation with the formation of mesityl oxide:



88. Comparison of Aldehyde and Ketone Properties. Both aldehydes and ketones can add hydrogen, sodium bisulphite (among the ketones this applies only to those that contain one methyl or two meth-

ylene groups in immediate proximity to the carbonyl), hydrogen cyanide, and organomagnesium compounds. With hydroxylamine and phenylhydrazine, aldehydes and ketones form oximes and phenylhydrazones. Phosphorus pentachloride causes an atom of oxygen in the aldehyde or ketone molecule to be replaced by two chlorine atoms (Table 7).

TABLE 7. Reactions of Aldehydes and Ketones

Reagent	Reaction products	
	with aldehydes	with ketones
hydrogen 2H sodium bisulphite	primary alcohols $R-GH_2OH$ aldehyde sodium bisulphite addition compounds	secondary alcohols $R-CH(OH)-R'$ ketone sodium bisulphite addition compounds
$NaHSO_3$	$\begin{array}{c} OH \\ \\ R-CH \\ \\ SO_3Na \end{array}$	$\begin{array}{c} R \\ \diagdown \\ C \\ \diagup \\ R' \\ \\ SO_3Na \end{array}$
hydrogen cyanide	cyanohydrins	cyanohydrins
HCN	$\begin{array}{c} OH \\ \\ R-CH \\ \\ CN \end{array}$	$\begin{array}{c} R \\ \diagdown \\ C \\ \diagup \\ R' \\ \\ CN \end{array}$
alkylmagnesium halide		
$R''-MgI$	$\begin{array}{c} OMgI \\ \\ R-C-R'' \\ \\ H \end{array}$	$\begin{array}{c} R \\ \diagdown \\ C \\ \diagup \\ R' \\ \\ OMgI \end{array}$
ammonia	aldehyde ammonias	complex reaction products
NH_3	$\left[\begin{array}{c} OH \\ \\ R-C-NH_2 \\ \\ H \end{array} \right]$	
hydroxylamine	aldoximes	ketoximes
NH_2OH	$R-CH=NOH$	$\begin{array}{c} R \\ \diagdown \\ C=NOH \\ \diagup \\ R' \end{array}$
hydrazine	aldehyde hydrazones	ketone hydrazones
NH_2-NH_2	$R-CH=N-NH_2$	$\begin{array}{c} R \\ \diagdown \\ C=N-NH_2 \\ \diagup \\ R' \end{array}$

Continuation

Reagent	Reaction products	
	with aldehydes	with ketones
phenylhydrazine	aldehydephenylhydra- zones	ketone phenylhydra- zones
$\text{C}_6\text{H}_5\text{NH}-\text{NH}_2$	$\text{R}-\text{CH}=\text{N}-\text{NH}-\text{C}_6\text{H}_5$	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_5 \\ \diagup \\ \text{R}' \end{array}$
phosphorus pentachlo- ride	dihalogen derivatives	dihalogen derivatives
PCl_5	$\text{R}-\text{CHCl}_2$	$\text{R}'-\text{CCl}_2-\text{R}''$
alcohol	acetals	ketone acetals are not formed in this way
$\text{R}'-\text{OH}$	$\begin{array}{c} \text{OR}' \\ \diagup \\ \text{R}-\text{CH} \\ \diagdown \\ \text{OR}' \end{array}$	
fuchsin-sulphurous acid	coloration	—
ammoniacal solution of silver oxide	"silver mirror"	—

There are several substantial differences between aldehydes and ketones. Unlike aldehydes, ketones do not produce a colouring of a colourless solution of fuchsin-sulphurous acid, are not resinified by alkalis, and do not add ammonia, but react with it (with the elimination of water and formation of several complex substances); nor do they form acetals with alcohols.

Ketones undergo oxidation less readily than aldehydes do; moreover, their oxidation breaks up the molecule. The condensation of ketones is also more difficult to bring about.

SOME REPRESENTATIVE ALDEHYDES AND KETONES

89. Formaldehyde. Formaldehyde $\text{H}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array}$ is a gas with a pungent odour. Its name is derived from formic acid. A 30-40% solution of formaldehyde is known as formalin. Formaldehyde was first prepared by Butlerov.

Industrially it is prepared by oxidizing methyl alcohol by the oxygen of the air. This is accomplished by passing a mixture of the

alcohol vapour and air over a copper catalyst at a high temperature. Once the reaction begins, the catalyst is heated by the reaction itself.

Fig. 33 shows a set-up for the laboratory preparation of formaldehyde by the catalytic oxidation of methyl alcohol.

The methyl alcohol is poured into a flask, which is placed in a jar of water, whose temperature is maintained at about 45-48°. After the copper spiral in the tube has been made very hot, air, dried

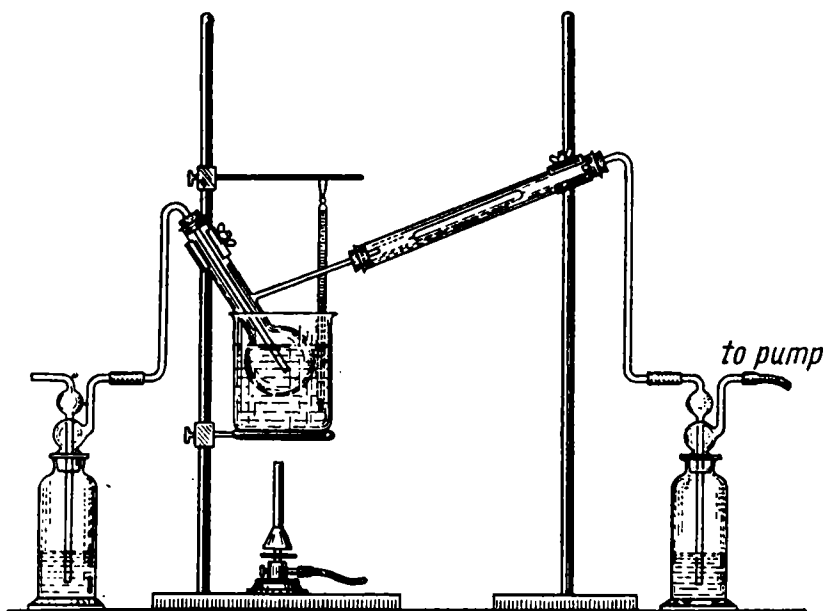
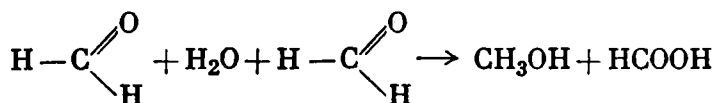


Fig. 33. Set-up for the catalytic oxidation of methyl alcohol.

in a wash-bottle with sulphuric acid, is sucked through the installation. The air entrains the alcohol vapour. After an interval of time fuchsin-sulphurous acid, poured into the right-hand wash-bottle, acquires a magenta colour, which points to the formation of an aldehyde. The spiral remains hot even when the flame is removed.

In chemical properties formaldehyde differs markedly from other aldehydes. Whereas most of the fatty aldehydes are resinified by alkalis, formaldehyde, when subjected to the action of an alkali, gives methyl alcohol and formic acid:

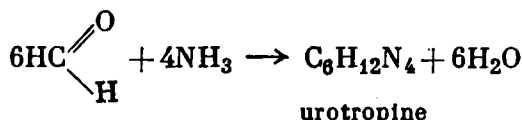


One molecule of formaldehyde is in this case oxidized, while another is reduced. This transformation of an aldehyde into an alcohol and an acid is known as the Cannizzaro reaction in honour of the

scientist who discovered it (1853). The Cannizzaro reaction is believed to play a significant part in many biological processes and to take place in natural conditions with the participation of enzymes.

With ammonia formaldehyde does not form an aldehyde ammonia; the reaction produces *urotropine*.

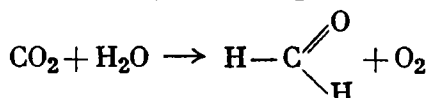
The over-all equation of the reaction is:



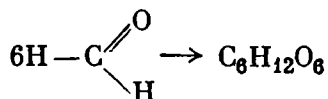
Urotropine is a white crystalline substance first prepared by Butleroy. It is employed medicinally as a urinary antiseptic and in the treatment of influenza. The action of nitric acid upon urotropine produces a powerful explosive, known as hexogen. Large quantities of urotropine are used in the manufacture of plastics.

When an aqueous solution of formaldehyde is evaporated carefully, polymerization takes place and a solid polymer, called *paraformaldehyde*, is formed. Its molecular weight is many times greater than that of formaldehyde. Heating reconverts paraformaldehyde to formaldehyde.

In 1870 Baeyer—proceeding from the experiments of Butlerov, the first to prepare a saccharoid substance by formaldehyde condensation—expressed the view that formaldehyde was the first-stage product of carbon assimilation by green plants:



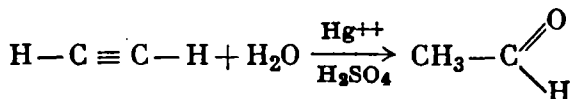
This reaction proceeds with the participation of chlorophyll and involves the absorption of the energy of sunlight. Subsequent polymerization converts the formaldehyde to carbohydrates:



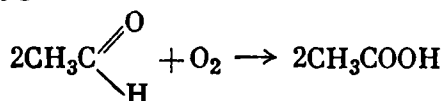
Formaldehyde serves as an initial material for preparing many substances that have extensive applications. With ammonia it forms urotropine, while with phenol and certain other substances it yields resins that serve to make plastic substitutes for horn, porcelain, gutta-percha, and metals. Formaldehyde is used to make certain dyes; it is also utilized in the manufacture of sole leather and water-proof fabrics, since with proteins it gives a product that does not swell in water.

Formaldehyde aqueous solution, formalin, is poisonous and is a strong disinfectant, used in the disinfection of premises and in grain treating (it kills smut balls). Formalin serves as a preservative of anatomical specimens.

90. Acetaldehyde. One of the industrial methods for preparing acetaldehyde is by the Kucherov reaction (p. 90):



Acetaldehyde is a liquid with a pungent odour, which boils at 21° . In the presence of catalysts, such as manganese salts, it is readily oxidized by the oxygen of the air to acetic acid:



A drop of concentrated sulphuric acid turns acetaldehyde into a substance boiling at 124° , i.e., at a much higher temperature than acetaldehyde does. This substance is called *paraldehyde*.

The vapour density of paraldehyde in relation to hydrogen is 66; consequently, its molecular weight is 132, whereas the molecular weight of acetaldehyde is 44. This can only mean that three molecules of acetaldehyde make up a molecule of paraldehyde.

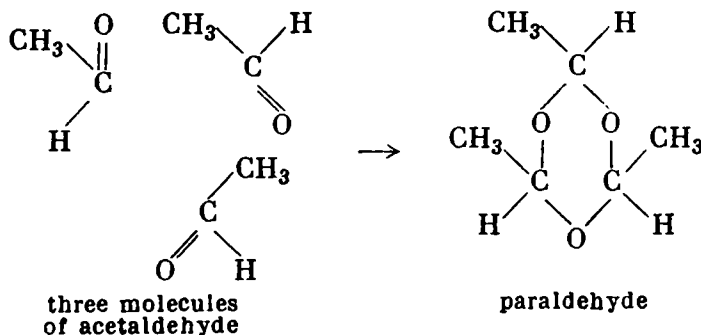
The properties of paraldehyde throw light on the manner in which the acetaldehyde molecules link up.

Paraldehyde does not exhibit the characteristic aldehyde reactions: it does not reduce an ammoniacal solution of silver oxide, does not impart a magenta colour to fuchsin-sulphurous acid, does not form phenylhydrazone, etc. This shows that its molecule does

not contain the $-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{H} \end{array}$ group typical of aldehydes.

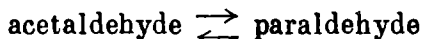
Heating with weak sulphuric acid depolymerizes paraldehyde to highly volatile acetaldehyde. This indicates that the links between the acetaldehyde molecules are not particularly strong. Inasmuch as bonds between carbon atoms are strong enough to withstand heating with weak sulphuric acid, it may be assumed that the acetaldehyde molecules are linked not via the carbon atoms, but via the oxygen atoms.

The formation of paraldehyde can be presented by the following equation:



The double bonds between the oxygen and carbon atoms in the acetaldehyde molecules are ruptured, and the free valency units acquired by these atoms are mutually saturated by three acetaldehyde molecules.

When paraldehyde or acetaldehyde is subjected to the action of sulphuric acid, a state of equilibrium arises:

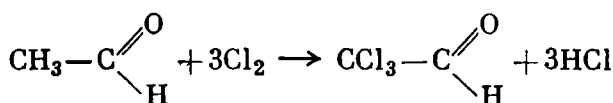


If a small quantity of concentrated sulphuric acid is added carefully to acetaldehyde at a low temperature, part of the acetaldehyde is turned into paraldehyde. If we now neutralize the acid with an alkali, it is easy to distil off the acetaldehyde from the paraldehyde. When a little sulphuric acid is added to the paraldehyde, part of it is turned into acetaldehyde. Heating vaporizes the acetaldehyde, causing it to leave the reaction sphere. As a result, the balance of the reaction is shifted from right to left, so that part of the paraldehyde is again turned into acetaldehyde, and so on.

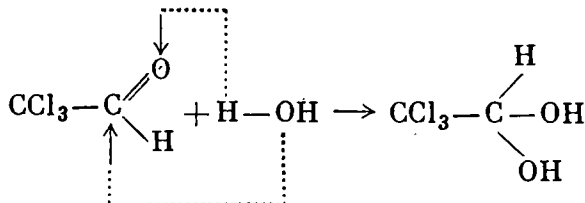
The action of sulphuric acid upon acetaldehyde at a low temperature produces another polymer: crystalline metaldehyde ($\text{C}_2\text{H}_4\text{O}$)₄. Like paraldehyde, metaldehyde can be depolymerized to acetaldehyde.

91. **Chloral** $\text{Cl}_3\text{C}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array}$. As stated above (p. 189), the α -hy-

drogen of aldehydes and ketones is exceptionally reactive, which is evidenced by the fact that the action of halogens easily brings about its replacement:



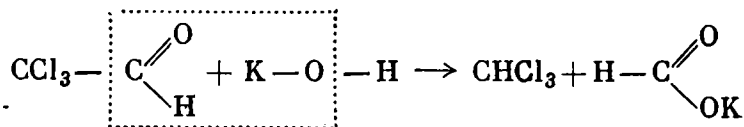
Chloral is an oily liquid (relative density 1.5) boiling at 98° . It is employed medicinally as a soporific. The addition of water to chloral produces heating and the formation of solid *chloral hydrate* $\text{CCl}_3-\text{CH}(\text{OH})_2$:



Chloral hydrate is one of the few stable substances with two hydroxyls attached to a single carbon atom.

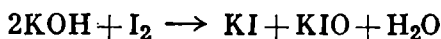
The three chlorine atoms in the chloral molecule considerably weaken the bond between the carbon atoms; for this reason the action

of aqueous alkali solutions upon chloral even at ordinary temperature break it up into chloroform and a formic acid salt:

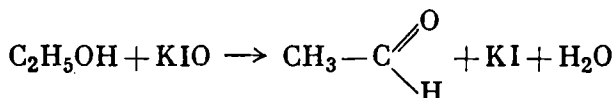


This reaction helps to understand the mechanism whereby iodoform and chloroform are formed from ethyl alcohol, an alkali, and a halogen.

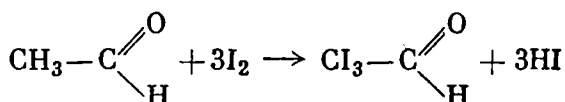
The action of potassium hydroxide on iodine produces potassium iodide and potassium hypoiodite KIO:



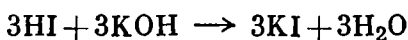
The potassium hypoiodite oxidizes the ethyl alcohol to acetaldehyde:



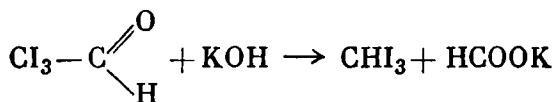
In the resulting acetaldehyde iodine replaces three hydrogen atoms to produce iodal:



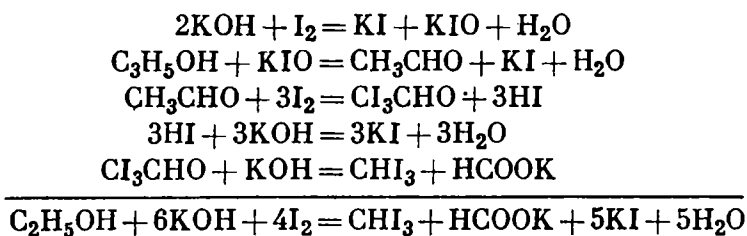
The potassium hydroxide neutralizes the hydrogen iodide:



And the excess alkali breaks up the iodal into iodoform and potassium formate:



By adding the equations of all these reactions, we obtain the over-all equation for the formation of iodoform:



This reaction is characteristic not only of acetaldehyde, but of all substances containing the $\text{CH}_3 - \text{C} -$ group, e.g., of all the methyl ketones. All of them in

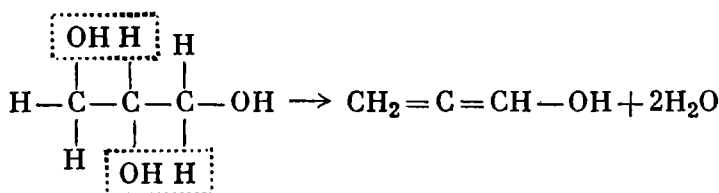
$$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$$

these conditions yield iodoform.

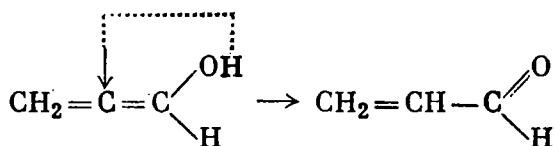
Chloroform is prepared similarly: by the action of an alkaline solution of chlorine or the action of calcium hypochlorite upon ethyl alcohol.

92. **Acrolein.** Acrolein (propenal) $\text{CH}_2=\text{CH}-\text{C}\begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix}$ is the simplest of the unsaturated aldehydes.

Acrolein is prepared by detaching two molecules of water from glycerol by means of dehydrating agents. Since the hydrogen and the hydroxyl are removed from neighbouring carbon atoms, the reaction should produce an alcohol with the hydroxyl attached to a doubly bound carbon atom:

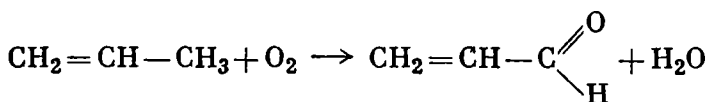


But such an alcohol is unstable; the moment it is formed it undergoes an isomeric transformation into an aldehyde:



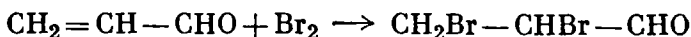
Acrolein is a colourless liquid boiling at 52° ; it has an extremely acrid odour, which accounts for its name (*acre* meaning sharp; *oleum*, oil). The formation of negligible amounts of acrolein is responsible for the acrid smell of burnt fats and oils.

Industrially acrolein is produced by the direct catalytic oxidation of propylene:



It finds application as an intermediate product in the industrial manufacture of synthetic glycerine and also in the manufacture of certain synthetic resins.

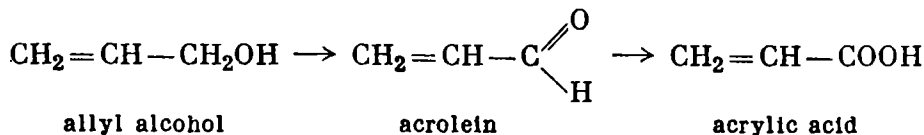
Chemically acrolein is highly reactive; this is due to the aldehyde group and the double bond in its molecule. It has a particularly pronounced tendency to add either to the aldehyde group or to the ethylene bond, or even to both. The action of bromine upon it, for example, produces dibromopropionic aldehyde:



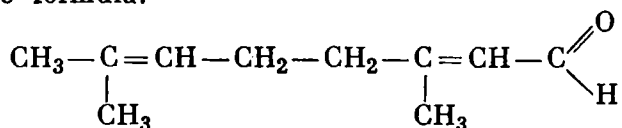
Acrolein adds hydrogen chloride to form 3-chloropropanal, i.e., the process does not obey Markovnikov's rule (p. 77). Acrolein polymerizes very readily to form a solid amorphous mass called *disacryl*.

The oxidation of acrolein by silver oxide gives acrylic acid $\text{CH}_2=\text{CH}-\text{COOH}$.

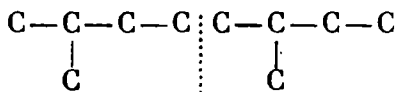
By oxidizing allyl alcohol in special conditions we can obtain acrolein, whose oxidation yields acrylic acid:



93. Citral. Another interesting unsaturated aldehyde is citral $\text{C}_{10}\text{H}_{16}\text{O}$, an oily liquid with a pleasant lemon odour (b.p. 228°). It occurs in many essential oils, e.g., lemon oil. The aldehyde nature of citral is confirmed by the fact that it can be prepared by the oxidation of the primary alcohol geraniol $\text{C}_{10}\text{H}_{18}\text{O}$ and can itself be oxidized to geranic acid $\text{C}_{10}\text{H}_{16}\text{O}_2$. The structure of citral is expressed by the formula:



The citral molecule thus appears to be made up of the carbon skeletons of two isopentane molecules:



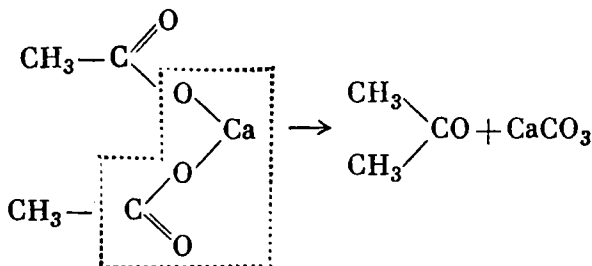
Such a structure of the carbon chain can be observed in a number of other natural compounds: rubber, terpenes, carotenoids, etc.

Citral is used in flavours and serves to synthesize ionone, an artificial violet scent.

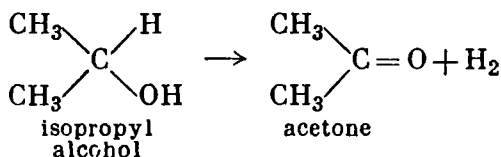
In recent years citral has become important as a drug reducing the blood pressure (in hypertension).

94. Acetone. Acetone $\text{CH}_3-\text{CO}-\text{CH}_3$ (propanone-2) is industrially the most important of the ketones.

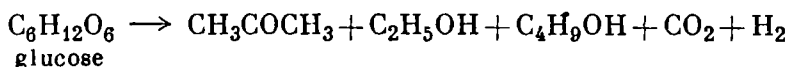
It is formed in the destructive distillation of wood, but is difficult to isolate from the other distillation products. For this reason it is prepared by decomposing calcium acetate, which is formed when acetic acid, likewise obtained from wood distillation, is neutralized with lime. When heated, calcium acetate decomposes, forming acetone and calcium carbonate:



This used to be practically the only source of acetone. It can also be prepared directly from acetic acid by passing the acid vapour over heated catalysts (Al_2O_3 , ThO_2). At present acetone is manufactured chiefly from petroleum cracking gases. Benzene is alkylated by propylene, and the resulting cumene is oxidized to give acetone and phenol (p. 416). Acetone is also prepared by dehydrogenating isopropyl alcohol, obtained from propylene. Isopropyl alcohol vapour is passed over metallic copper or zinc oxide:



Acetone can be prepared from starch by fermentation caused by the mould *Clostridium acetobutylicum*. Fermentation at first saccharifies the starch to glucose, and this is then converted to acetone, ethyl alcohol, and butyl alcohol, with large amounts of carbon dioxide and hydrogen being evolved:



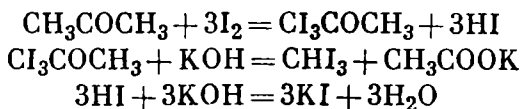
An exact equation cannot be written for this reaction, which is highly complex and has not been studied sufficiently. The liquid products consist of about 60% acetone, 30% ethyl alcohol, and 10% butyl alcohol; the gases evolved consist of 60% carbon dioxide and 40% hydrogen. The raw material used is cereal or potato starch or, most frequently, maize.

Acetone is a light liquid boiling at 56° ; it has a characteristic odour and is an excellent solvent for many substances. It is completely miscible with water. If a solution of potash is added to an aqueous solution of acetone, the liquid separates into two layers: the lower layer is an aqueous solution of potash with a small amount of acetone, while the upper layer consists chiefly of acetone. This is known as salting out acetone.

Since acetone, like acetaldehyde, contains the $\text{CH}_3\text{—C—}$ group,



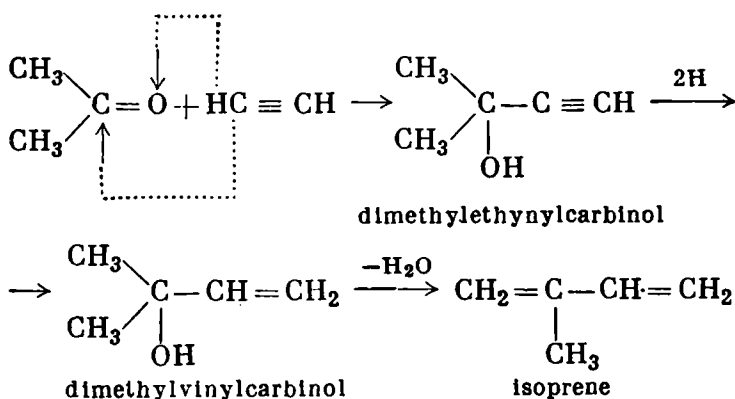
it too reacts with iodine and an alkali to produce iodoform. The reactions that take place may be expressed by the following equations:



Acetone has many applications. It is used in the manufacture of chloroform and iodoform and as a solvent in the production of lacquers, non-flam film, and a type of artificial silk (acetate rayon). Acetone is also used as a solvent for acetylene, as a gelatinizer in gunpowder manufacture, and as a starting material in the industrial production of several organic substances.

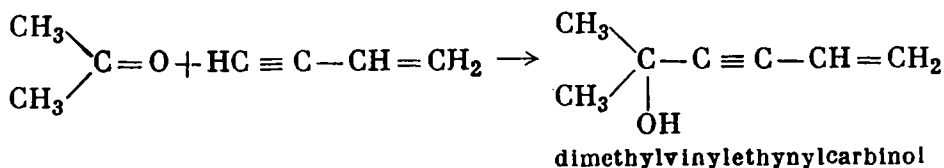
Chlorine and bromine derivatives of acetone have a pronounced lachrymatory action and were used in the war of 1914-18 as chemical warfare agents.

A reaction that has acquired considerable importance lately is the condensation of acetone with hydrocarbons containing a triple bond. It was discovered by Favorsky, who demonstrated that the acetylene hydrocarbons can, in the presence of powdered potassium hydroxide, condense with aldehydes and ketones to form acetylene alcohols. For example, in the presence of potassium hydroxide, acetylene and acetone yield dimethylethynylcarbinol*, its electrolytic hydrogenation produces dimethylvinylcarbinol. The removal of the elements of water from the latter gives isoprene:



The polymerization of isoprene produces synthetic rubber (p. 97 fol.)

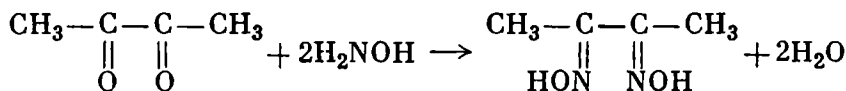
The condensation of vinylacetylene with acetone in the presence of potassium hydroxide yields dimethylvinylethynylcarbinol:



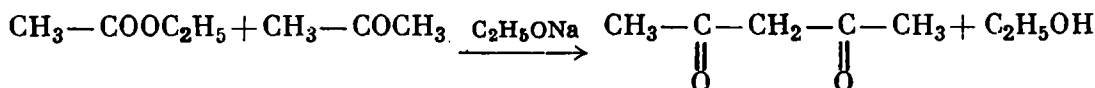
I. Nazarov developed a technique for obtaining vinylacetylene resins from this alcohol. These resins have extensive applications as adhesives ("carbinol glue") for a variety of materials (glass, minerals plastics, metals) and in the production of lacquers.

* The name ethynyl has been given to the radical $\text{CH} \equiv \text{C}-$.

ylamine upon diacetyl produces a dioxime, *dimethylglyoxime* (m.p. 240°):

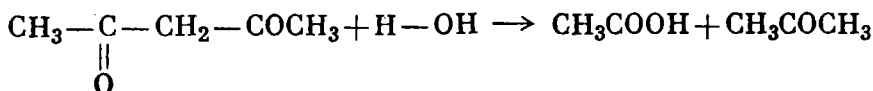


Acetylacetone, or β -diketone, is prepared by the Claisen reaction, the condensation of ethyl acetate and acetone in the presence of sodium alcoholate:

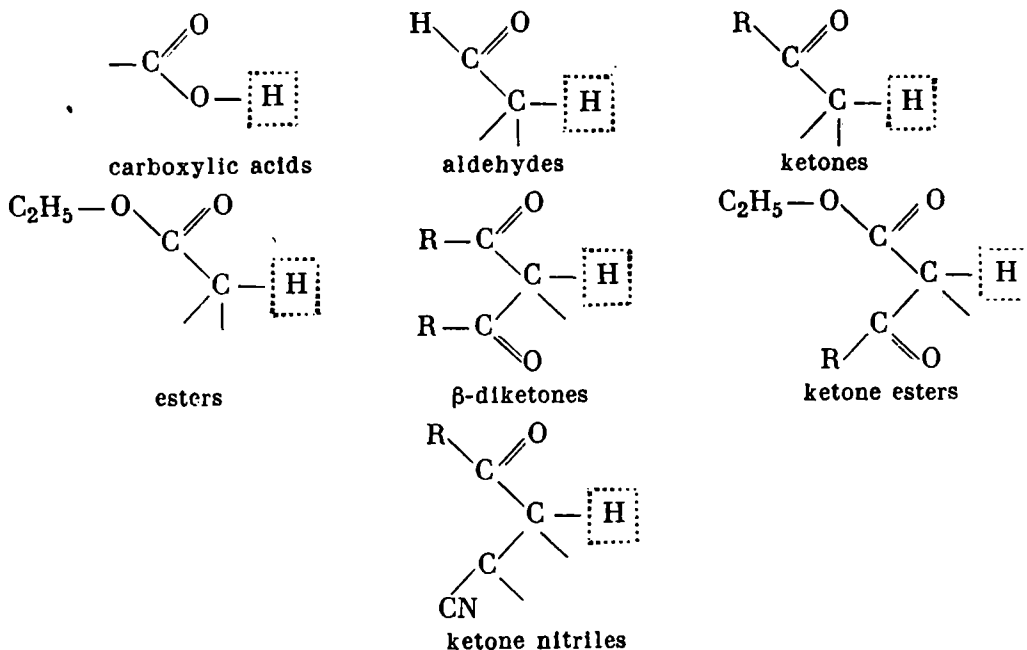


The Claisen reaction is discussed in greater detail on p. 283.

Acetylacetone is a liquid with a characteristic odour; it boils at 137°. When boiled with water, acetylacetone decomposes, yielding acetic acid and acetone:

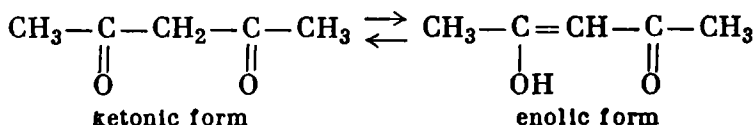


As pointed out earlier (p. 189), the carbonyl group makes the α -hydrogen atoms reactive. This influence of the carbonyl can be traced in nearly all the carbonyl-containing compounds:



The β -ketones contain two carbonyl groups, and the α -hydrogen atoms next to these groups are, accordingly, even more mobile. In

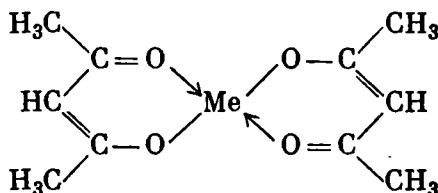
a solution of acetylacetone there is a state of equilibrium:



Compounds with a hydroxyl group (ol) attached to a doubly bound carbon atom (ene) are called *enols*. This type of chemical structure exhibits several distinctive features.

By physico-chemical methods it has been established that the equilibrium in the case of acetylacetone is shifted in the direction of the enolic form (the solution contains 23.6% of the diketone and 76.4% of the enol).

96. Chelate Compounds. With copper, nickel, and beryllium, and also with aluminium, chromium, iron, and other elements, acetylacetone forms compounds of the structure:



In this case the enolic form of acetylacetone reacts with the metal salts or their hydroxides in such a way that the metal is linked covalently to the hydroxyl group residue and coordinately to the carbonyl oxygen.

The result is a cyclic compound containing the metal in its cycle. Such compounds are called *chelate* or *inner-complex compounds*, and they are very different from typical salts with ionic bonds between the metal cation and the anion (p. 342).

Chelate compounds have the following properties:

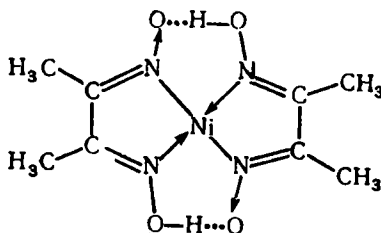
(1) They dissolve readily in organic solvents (with a characteristic coloration) and do not dissolve in water.

(2) They are very weakly ionized, i.e., are non-electrolytes.

(3) Many of them can be sublimed and distilled without decomposing.

(4) They often have bright colours, distinct from the colours of the ordinary salts of the same metal.

All these properties are exhibited by the chelate compound of nickel with dimethylglyoxime (p. 203):



Thanks to its four five-membered cycles, the compound is stable. The reaction between dimethylglyoxime and the salts of nickel was discovered in 1906 by L. Chugayev. It is used extensively for the qualitative detection and quantitative estimation of nickel (in the presence of cobalt) and several other metals.

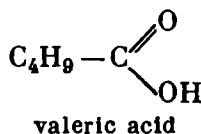
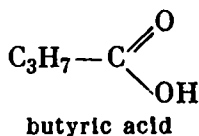
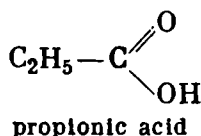
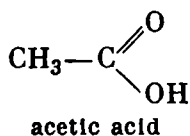
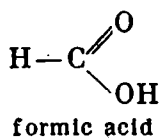
Chelate compounds are very much in use in analytical chemistry as reagents; they are also used in producing metals of a high degree of purity.

Carboxylic Acids and Their Derivatives

SATURATED MONOCARBOXYLIC ACIDS

97. Structure and Preparation of Carboxylic Acids. The molecules of the carboxylic acids contain the $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C} \\ \backslash \\ \text{OH} \end{array}$ or $-\text{COOH}$ group of atoms, called the *carboxyl*.

The following are examples of carboxylic acids:



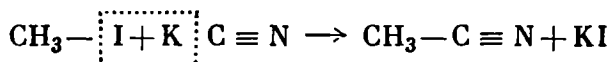
The structural formula of this group and even its very name *carboxyl* indicate that it is, so to say, a combination of the carbonyl group $>\text{C}=\text{O}$ and the hydroxyl group $-\text{OH}$. However, the ketone or aldehyde character of the $>\text{C}=\text{O}$ group is not manifested in the carboxyl in any way. The oxygen atoms of the carboxyl are perfectly identical. This is borne out by investigations of the physical properties of the carboxylic acids and their X-ray spectra.

The basicity of an acid is determined by the number of carboxylic groups in its molecule: acetic acid CH_3-COOH is monocarboxylic, while oxalic acid $\text{HOOC}-\text{COOH}$ is dicarboxylic.

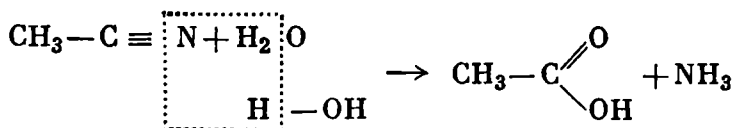
The composition of the saturated monocarboxylic acids is expressed by the formula $\text{C}_n\text{H}_{2n+1}-\text{COOH}$; they form a typical homologous series.

There are a number of methods for preparing carboxylic acids.

1. *Hydrolysis of Nitriles.* The action of potassium cyanide on methyl iodide produces methyl cyanide (a liquid boiling at 81.5°):

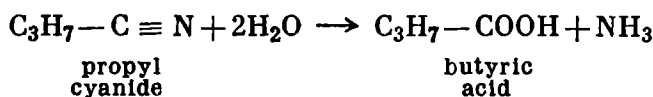
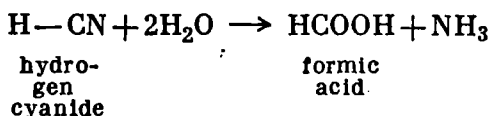


When heated with dilute inorganic acids, methyl cyanide adds water and breaks up into ammonia and acetic acid:



If, on the other hand, methyl cyanide is heated with alkalis, ammonia and sodium acetate are produced.

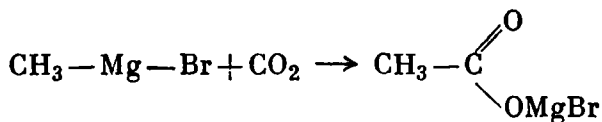
Other acids can be produced similarly:



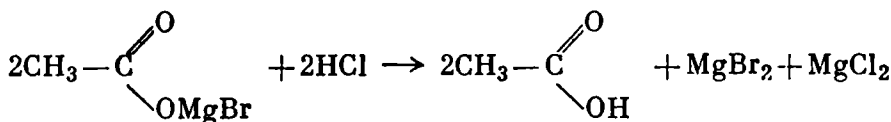
As seen from the above, formic acid can be prepared from hydrogen cyanide.

Hydrolysis turns the alkyl cyanides into acids with the same number of carbon atoms; for this reason they are called *acid nitriles*: methyl cyanide or acetonitrile, ethyl cyanide or propionitrile. This reaction confirms the structure of acids.

2. *Action of Carbon Dioxide on Organomagnesium Compounds.* The action of carbon dioxide on methylmagnesium bromide gives an addition product:

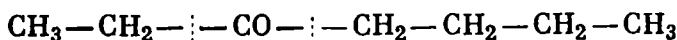


This product may be regarded as a mixed salt of acetic acid and hydrobromic acid. The treatment of this salt with a mineral acid produces acetic acid:



3. The preparation of acids by means of malonic ester and acetoacetic ester is described on pp. 254 and 286.

4. *Oxidation of Organic Substances.* Saturated monocarboxylic acids can be prepared by the oxidation of many organic compounds. This is often attended by the breakdown of molecules, so that the resulting acid contains fewer carbon atoms than the initial compound. For instance, the oxidation of ethyl butyl ketone



can yield:

acetic acid $\text{CH}_3\text{—COOH}$

propionic acid $\text{CH}_3\text{—CH}_2\text{—COOH}$

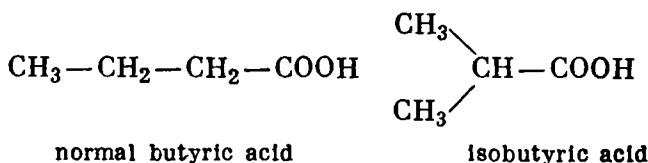
n-butyric acid $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—COOH}$

n-valeric acid $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—COOH}$

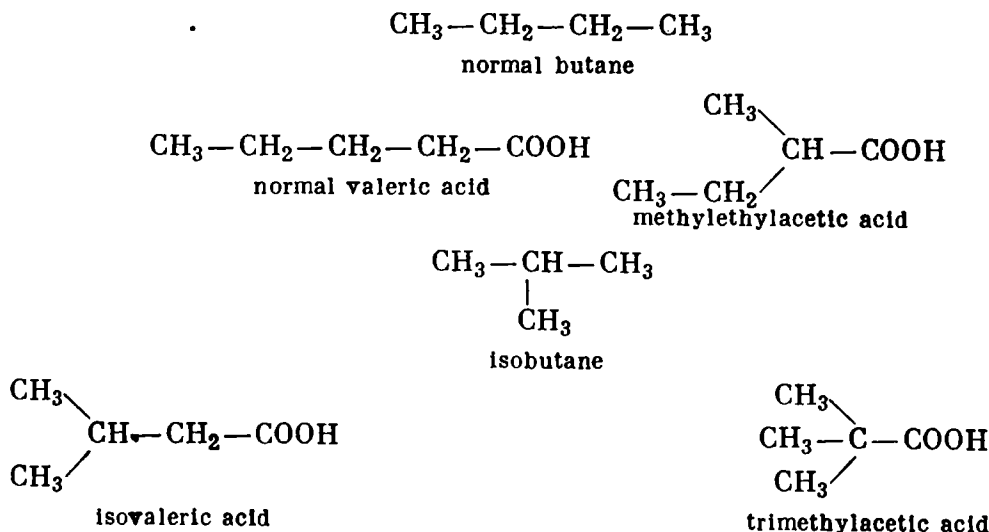
The oxidation of primary alcohols (p. 137) and aldehydes (p. 185) gives acids with the same number of carbon atoms in the molecule. Many acids can also be prepared from vegetable and animal matter.

98. Isomerism and Nomenclature of Saturated Monocarboxylic Acids. The saturated monocarboxylic acids, which come under the general formula $\text{C}_n\text{H}_{2n+1}\text{—COOH}$, are often called fatty acids, because members of this series were first prepared from fats.

Formic acid H—COOH may be regarded as a compound of hydrogen with the carboxyl. Acetic acid $\text{CH}_3\text{—COOH}$ is a carboxylic derivative of methane CH_4 ; propionic acid $\text{C}_2\text{H}_5\text{—COOH}$ is a carboxylic derivative of ethane C_2H_6 . Since all the hydrogen atoms in the methane and ethane molecules are equivalent, it makes no difference which of these atoms is replaced by a carboxyl; acetic acid and propionic acid therefore have no isomers. But in the case of the fourth member of the series, butyric acid, two isomers are possible:



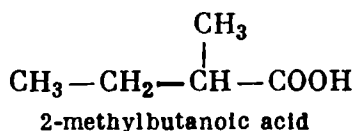
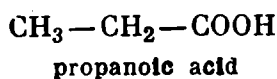
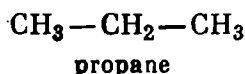
In the case of valeric acid four isomers are possible and are actually known. Two of them may be looked upon as derivatives of normal butane, and the two others, as derivatives of isobutane:



Whereas alcohols may be regarded as hydrocarbons in which one hydrogen atom has been replaced by a hydroxyl, acids may be looked upon as hydrocarbons in which one hydrogen atom has been replaced by a carboxyl. By substituting a carboxyl for a hydrogen atom, we are introducing a new carbon atom into the molecule; therefore, the number of isomeric carboxylic acids with n carbon atoms in the molecule is equal to the number of isomeric alcohols with $n - 1$ carbon atoms in the molecule.

In the Geneva nomenclature the names of acids are derived from the names of the hydrocarbons with the same number of carbon atoms in the molecule, to which the word "acid" is added. Formic acid $\text{H}-\text{COOH}$ is called methanoic acid, acetic acid CH_3-COOH is called ethanoic acid, etc.

The Geneva system in this way treats acids as derivatives of hydrocarbons, with one unit turned into a carboxyl:



In the commonly used nomenclature acids with branched carbon atom chains are often viewed as derivatives of acetic acid CH_3COOH , in whose molecule methyl group hydrogen atoms have been replaced by radicals: methylethylacetic acid, trimethylacetic acid.

The names most frequently used, however, are the traditional names, which usually refer to the material from which the particular acid was prepared, e.g., formic acid, acetic acid, butyric acid (first obtained from butter), valeric acid (obtained from the valerian root), lauric acid (from the fruit of the laurel tree), etc.

99. Physical Properties of Saturated Monocarboxylic Acids. The first four of the fatty acids are mobile liquids, miscible with water in all proportions. The acids whose molecules contain from five to nine carbon atoms (as well as isobutyric acid) are oily and have a low water-solubility.

The higher acids are solids and are practically insoluble in water; distillation at ordinary pressure causes them to decompose.

Formic, acetic, and propionic acids have sharp odours; the intermediate members of the series have unpleasant odours, and the higher acids are odourless. The principal physical properties of the saturated monocarboxylic acids are listed in Table 8.

The data in Table 8 show that with an increase in molecular weight there is a rise of the boiling point and decline of the relative density. Whereas the boiling points of the fatty acids rise smoothly with the

TABLE 8. Physical Properties of Saturated Monocarboxylic Acids

Acid	Formula	M.p. °C	B.p. °C	d_4^{20}
Formic acid	HCOOH	8.25	100.5	1.2322
Acetic acid	CH ₃ COOH	−16.6	118.5	1.049
Propionic acid . . .	CH ₃ CH ₂ COOH	−20.7	141.1	0.9916
Butyric acid	CH ₃ CH ₂ CH ₂ COOH	−3.11	163	0.959
Isobutyric acid . . .	(CH ₃) ₂ CHCOOH	−47	154.4	0.949
Valeric acid	CH ₃ (CH ₂) ₃ COOH	−34.5	186	0.9387
Caproic acid	CH ₃ (CH ₂) ₄ COOH	−1.5	205.3	0.922
Enanthic acid . . .	CH ₃ (CH ₂) ₅ COOH	−10.5	223	0.9184
Caprylic acid	CH ₃ (CH ₂) ₆ COOH	16.2	237.5	0.910
Pelargonic acid . . .	CH ₃ (CH ₂) ₇ COOH	12.5	253	0.9057
Capric acid	CH ₃ (CH ₂) ₈ COOH	31.5	268.4	0.8858
				(at 40°)
Undecylic acid . . .	CH ₃ (CH ₂) ₉ COOH	30.5	280	0.8907
				(at 30°)
Lauric acid	CH ₃ (CH ₂) ₁₀ COOH	44.3	225	0.8740
			(at 100 mm)	(at 42°)
Tridecoic acid . . .	CH ₃ (CH ₂) ₁₁ COOH	42.0	236	—
			(at 100 mm)	
Miristic acid	CH ₃ (CH ₂) ₁₂ COOH	53.7	250.5	0.8533
			(at 100 mm)	(at 70°)
Pentadecoic acid . .	CH ₃ (CH ₂) ₁₃ COOH	52.1	257	—
			(at 100 mm)	
Palmitic acid	CH ₃ (CH ₂) ₁₄ COOH	62.6	271.5	0.849
			(at 100 mm)	(at 70°)
Margaric acid* . . .	CH ₃ (CH ₂) ₁₅ COOH	60.8	277	0.848
			(at 100 mm)	(at 70°)
Stearic acid	CH ₃ (CH ₂) ₁₆ COOH	69.4	287	0.848
			(at 100 mm)	(at 70°)

* Margaric acid has not been found in natural products and has no direct connection with margarine. It was prepared synthetically by N. Demyanov and S. Kochergir.

increase in the number of carbon atoms in the molecule, their melting points exhibit a curious aberration: the melting point of an acid with an even number of carbon atoms in the molecule is higher than the melting points of both neighbouring acids with odd numbers of carbon atoms. This peculiarity is shown graphically in Fig. 34.

The determination of acid molecular weights reveals that in the liquid state they have doubled molecules. The vapour density of ace-

tic acid at low temperatures is greater than 30 and less than 60, i.e., the vapour is a mixture of single and double molecules. With a rise in temperature the vapour density diminishes, but only at a temperature exceeding 250° does it become equal to 30. Molecular association is thus even more pronounced in acids than in alcohols (p. 132).

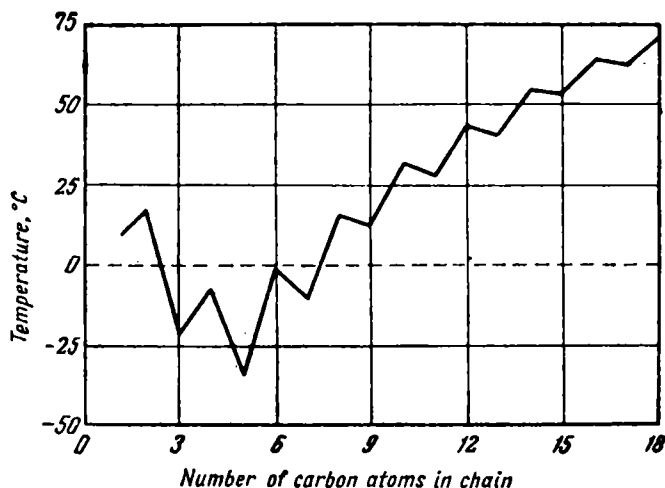


Fig. 34. Melting points of saturated monocarboxylic acids of normal structure.

Bragg studied the crystals of stearic, lauric, and other high-molecular acids by X-ray techniques. He found that the molecules in the crystals of these acids are situated in rows at a slight angle to the cleavage plane, i.e., the plane along which the crystal splits (Fig. 35). These rows of molecules form double layers; in each layer the molecules of two rows face each other with their carboxyl groups and are firmly linked by their auxiliary valencies. The molecules of different layers are in contact along the cleavage plane through their methyl groups, which do not form strong linkages. This accounts for the slipping of the crystals of fatty acids and fats.

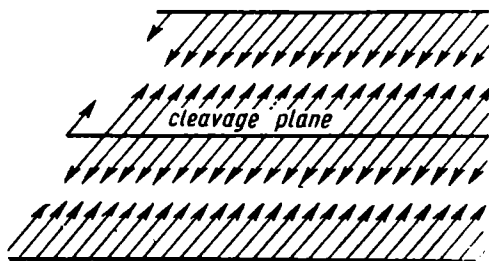
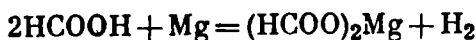
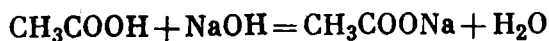


Fig. 35. Position of carbon chains in lauric acid crystal.

100. Chemical Properties of Saturated Monocarboxylic Acids. 1. The carboxylic acids have an acid reaction (which can be detected by indicators) and form salts with alkalis and alkaline metals:



Like alcohol molecules, acid molecules contain hydroxyl groups. Alcohols do not, however, exhibit acid properties, while in acids the hydroxyl hydrogen has all the properties of an acid hydrogen atom.

The acid properties of the hydroxyl are more pronounced in acids because of the influence exerted upon it by the oxygen of the carbonyl group, with whose carbon atom the hydroxyl is directly linked.

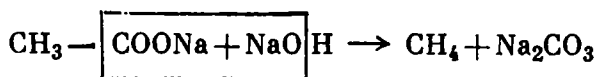
Most carboxylic acids dissociate very slightly in aqueous solutions and are weak acids, not nearly as strong as hydrochloric, nitric, or sulphuric acid. When 1 g-mol is dissolved in 16 l of water, the degree of dissociation of formic acid is 0.06 and of acetic acid 0.0167, whereas hydrochloric acid is dissociated almost completely in such a dilute state.

Table 9 lists the ionization constants of some of the fatty acids.

TABLE 9. Ionization Constants of Some Fatty Acids

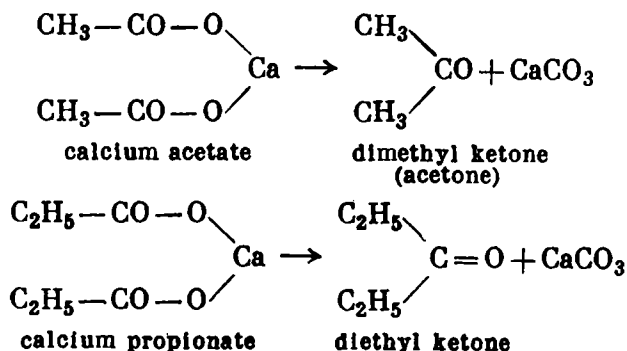
Acid	Dissociation constant	Acid	Dissociation constant
Formic acid . . .	214×10^{-6}	Butyric acid . .	15.2×10^{-6}
Acetic acid . . .	17.6×10^{-6}	Valeric acid . .	16.0×10^{-6}
Propionic acid . .	13.4×10^{-6}	Caproic acid . .	13.8×10^{-6}

2. When alkaline metal salts of the fatty acids are fused with alkalis, the carbon chain is ruptured and a hydrocarbon is formed from the hydrocarbon radical of the acid:



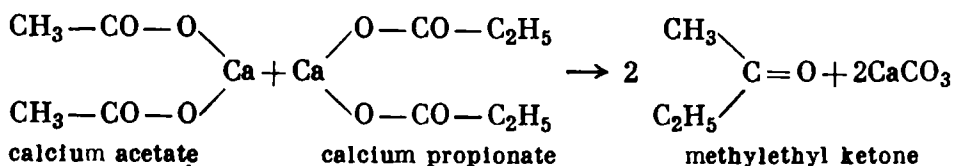
3. The dry distillation of calcium and barium salts of the fatty acids (with the exception of formic acid salts) yields symmetric ketones.

The distillation of calcium acetate yields dimethyl ketone; the distillation of calcium propionate yields diethyl ketone:

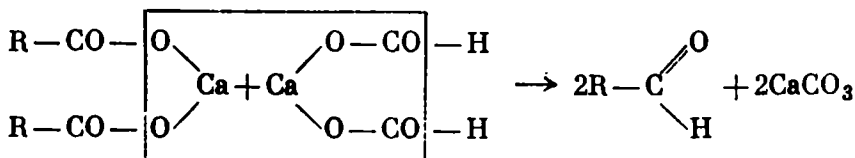


When a mixture of salts of two different acids is taken, the above reaction is not the only one: there is also a reaction between the two different salt molecules, which gives rise to ketones with two different radicals.

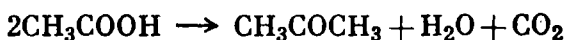
When, for example, we distil a mixture of calcium acetate and calcium propionate, we obtain methylethyl ketone, as well as dimethyl ketone CH_3COCH_3 and diethyl ketone $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$:



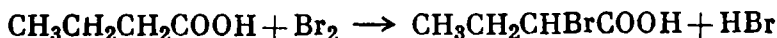
But if one of the salts in the mixture taken is a formate, we obtain an aldehyde:



Ketones will also be formed if, instead of distilling the salts, we pass the vapours of the acids over heated catalysts (thorium dioxide, calcium carbonate, etc.). Aldehydes will result if manganese oxide or titanium dioxide is taken as a catalyst. Salts are presumably formed as intermediate products, but are then decomposed, so that the initial catalyst is regenerated. When, for instance, acid vapours are led over calcium carbonate, the products are a calcium salt of a carboxylic acid, water, and carbon dioxide. The calcium salt decomposes to form a ketone and calcium carbonate; the interaction of the latter with the acid again yields a calcium salt, water, and carbon dioxide, etc. The result of the reaction may be expressed by the following equation:



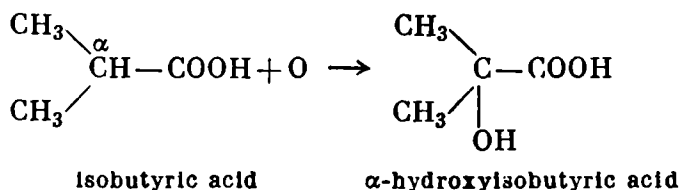
4. The hydrogen atoms of the acid hydrocarbon radical are chemically similar to the hydrogen atoms of the paraffins. The most reactive hydrogen atoms, however, are those attached to the carbon atom directly linked to the carboxyl. This is borne out most strikingly by the chlorination and bromination of the fatty acids. The action of chlorine or bromine, in the presence of halogen carriers (PCl_3 , I_2 , etc.), on fatty acids or their chlorides results in the replacement of the α -hydrogen atoms:



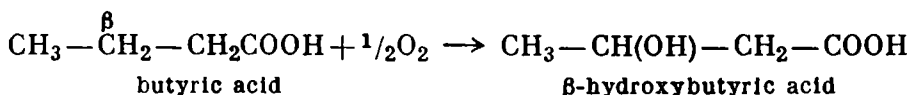
The carboxyl, like the carbonyl, makes the α -hydrogen atoms more reactive.

This was first noted by V. Markovnikov.

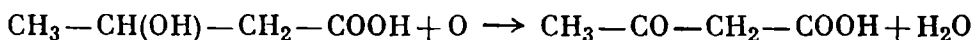
5. The fatty acids are, as a rule, stable with respect to oxidizing agents. Only formic acid and acids with tertiary carbon atoms are oxidized readily. The latter yield hydroxy acids, i.e., substances which are both alcohols and acids:



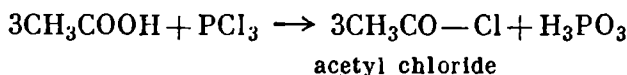
The fatty acids are capable of undergoing oxidation in the organism; the oxygen in this case goes into β -position, i.e., to the carbon atom separated from the carboxyl by another carbon atom. In the organisms of diabetes patients, for instance, butyric acid is converted into β -hydroxybutyric acid:



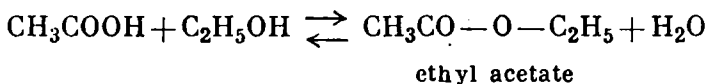
The oxidation of butyric acid has been achieved in the laboratory by using a 3% solution of hydrogen peroxide. The butyric acid is converted into β -hydroxybutyric acid (which contains a secondary alcohol group), and this upon further oxidation yields acetoacetic acid:



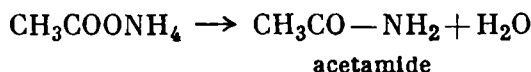
6. The action of halogen compounds of phosphorus upon acids produces acid halides (p. 245):



7. With alcohols acids yield esters (p. 233):



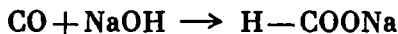
8. The heating of ammonium salts of acids gives amides (p. 248):



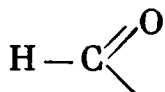
101. Formic Acid. Formic acid $\text{H} - \text{COOH}$ occurs in the gland secretions of certain species of ants, e.g., the red ant *Formica rufa*. This accounts for the Latin name of the acid: *acidum formicum*. Its salts are called *formates*.

Formic acid used to be obtained by treating ants with steam. Nowadays it is prepared by the action of carbon monoxide on sodium

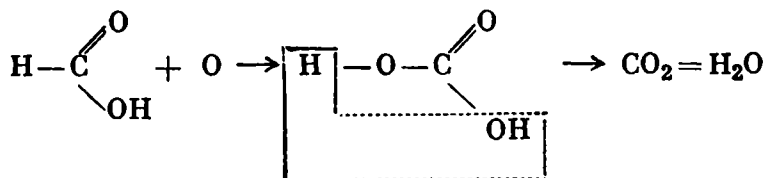
hydroxide at increased temperature and pressure; the reaction gives sodium formate:



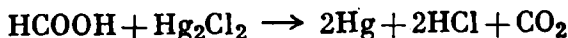
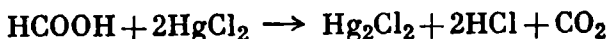
Formic acid is a colourless, sharp-smelling liquid with an acerbic taste. As may be seen from its structural formula ($\text{H}-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}$), formic acid differs structurally from the rest of the acids: its molecule contains a carbonyl linked to hydrogen, i.e., the aldehyde group



1. Like aldehydes and unlike the other carboxylic acids, formic acid is easily oxidized by oxidizing agents (KMnO_4 , CrO_3 , etc). Oxidation produces carbon dioxide and water:



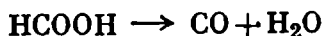
When we heat a solution of mercuric chloride acidified with formic acid, the mercuric chloride is reduced first to calomel and then to metallic mercury:



When mercuric formate is heated, the mercury is reduced to a free metal, while half the carbon is oxidized to carbon dioxide:



2. Concentrated sulphuric acid decomposes formic acid to carbon monoxide and water:



3. Formic acid is quite a strong acid; in aqueous solution it undergoes considerable ionization (Table 9, p. 212).

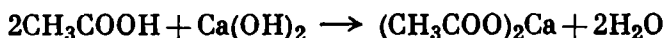
Formic acid is used in industry to produce oxalic acid.

102. Acetic Acid. Acetic acid CH_3-COOH is widespread in nature; it occurs as free acid in the human urine and sweat. Acetic acid esters are present in many plants.

Until recently the acid was prepared by two methods: the destructive distillation of wood and the bacterial oxidation of alcoholic

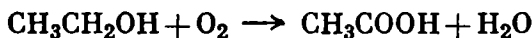
liquids ("quick vinegar fermentation"). In the former method the raw material is wood pulp; in the latter case, ethyl alcohol.

In wood distillation the acetic acid collects in the pyroligneous liquor. To separate the acetic acid from the methyl alcohol and acetone, it is neutralized by lime; the resulting calcium acetate, sometimes called "vinegar powder", is decomposed by hydrochloric or sulphuric acid:



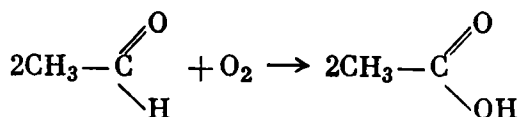
At some plants the acetic acid is extracted from the pyroligneous liquor by solvents (ethyl ether, ethyl acetate, etc.). The solvent is distilled off and can be used again for acetic acid extraction.

The quick vinegar fermentation of alcoholic liquids consists in oxidizing the ethyl alcohol to acetic acid by special bacteria, *Mycoderma acedi*. These bacteria, which multiply on the surface of the alcohol, oxidize it at the expense of oxygen in the air to acetic acid:



Since the bacteria need nitrogen- and phosphorus-containing food, the fermentation will take place in grape juice, wine, and beer, but not in aqueous solutions of pure alcohol, which contain no nitrogen or phosphorus compounds.

Industrially acetic acid is mainly produced by oxidizing acetaldehyde by the oxygen of the air in the presence of manganese catalysts:



As said above (p. 90), acetaldehyde is produced either from ethylene or from acetylene. The latter method is gradually losing its significance.

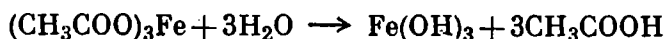
Recent years have seen the development of industrial methods of acetic acid production by the oxidation of hydrocarbons, such as butane, pentane, or the hexanes (N. Emanuel et al.).

Anhydrous acetic acid is a crystalline substance melting at 16.5°. The crystals resemble ice in appearance. For this reason 100% acetic acid is called *glacial acetic acid*. Crystalline acetic acid was first prepared by T. Lovits.

Commercial vinegar essence contains 70-80% of acetic acid; table vinegar is a 3-5% solution of acetic acid.

Like most carboxylic acids, acetic acid is a weak acid. Many of its salts are therefore easily hydrolyzed, i.e., decomposed by water.

Hydrolysis leads to the formation of a metal hydroxide and basic acetates:



Acetic acid and its salts, called *acetates*, have many applications.

Acetic acid is used as a seasoning in food and as a preservative for meat and fish products; acetic anhydride (p. 247), which is prepared from it, is used in the manufacture of artificial silk (acetate rayon); monochloroacetic acid $\text{CH}_2\text{Cl}-\text{COOH}$ (prepared by the chlorination of acetic acid) is used in enormous quantities to make the dye indigo; acetic acid serves to synthesize many flavours and solvents; it is employed in the tanning, textile, and other industries. The most commonly used acetates are the salts of iron, aluminium, and chromium, which are utilized as mordants in dyeing fabrics.

Lead acetate $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$, known as *sugar of lead*, is used to make white lead; it is highly poisonous.

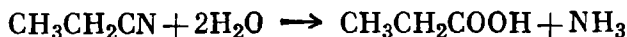
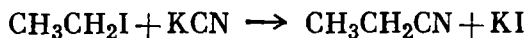
Basic lead acetate $(\text{CH}_3\text{COO})_2\text{Pb} \cdot \text{Pb}(\text{OH})_2$, or *Acetum Plumbi*, is used medicinally as Goulard's lotion.

Basic cupric acetate, known as *green verdigris*, is used as a green pigment.

A compound of cupric acetate with cupric arsenite, known as Paris green, is used as an insecticide for killing field, forest, and garden pests. This is achieved by spraying Paris green in the dry state or as a suspension in water.

Calcium acetate is used to make acetone (p. 199).

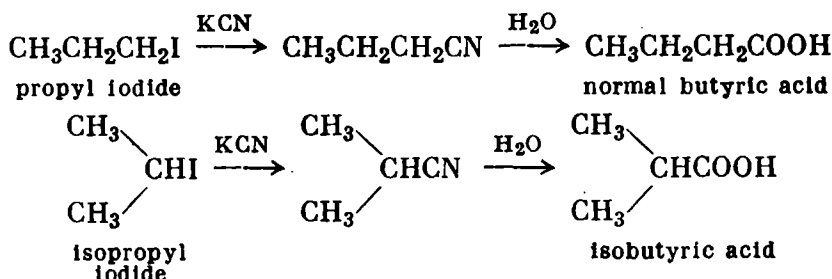
103. Propionic acid. Propionic (propanoic) acid can be prepared by the oxidation of *n*-propyl alcohol or by the action of potassium cyanide on ethyl iodide with the subsequent saponification of the resulting ethyl cyanide:



The name of the acid is derived from the Greek words *protos* and *pio* meaning "first fat"; it is the first member of this series producing a calcium salt that feels greasy.

104. Butyric Acid. Both of the theoretically possible butyric acid isomers are known: normal butyric acid (butanoic acid) and isobutyric acid (methylpropanoic acid). The structure of the former is confirmed by its preparation from propyl iodide; the structure of the

latter, by its preparation from isopropyl iodide:



The calcium salt of normal butyric acid, unlike the calcium salt of isobutyric acid, dissolves in cold water better than in hot water.

The isomerism of these acids was discovered in 1865 by Markovnikov, who demonstrated that the acid resulting from the oxidation of butyl alcohol, which boils at 108° , is not identical with ordinary butyric acid. He prepared this acid from isopropyl iodide and thereby established its structure and the structure of the alcohol from which it is derived by oxidation.

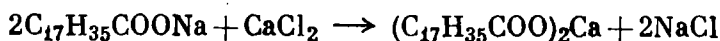
Normal butyric acid was isolated by M. Chevreul in 1814 from butter, in which it is contained in the form of an ester of glycerol. At present it is prepared by the fermentation of sugar under the influence of certain moulds, e.g., *Bacillus butyricus*. It has a disagreeable odour of rancid butter; it is used in making certain flavours and elsewhere.

105. Palmitic and Stearic Acids. Palmitic acid $\text{C}_{15}\text{H}_{31}\text{COOH}$, whose structure is expressed by the formula $\text{CH}_3-(\text{CH}_2)_{14}-\text{COOH}$, and stearic acid $\text{C}_{17}\text{H}_{35}\text{COOH}$, whose structural formula is $\text{CH}_3-(\text{CH}_2)_{14}-\text{COOH}$, occur with unsaturated acids (oleic, etc.) in nature as esters of glycerol, or glycerides, which are basic components of vegetable and animal fats. A mixture of stearic and palmitic acids is called *stearin*.

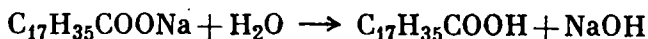
The salts of high-molecular organic acids are called *soaps*. Ordinary soap consists essentially of a mixture of sodium salts of palmitic, stearic, and oleic acids.

Potassium soap is of a glutinous appearance and is known as liquid soap. With the addition of a green pigment (if made from hempseed oil, the soap has a natural green colour) it is used medicinally as an antiseptic, known as *green soap*.

The calcium salts of the above acids are insoluble in water. Owing to this, in hard water, i.e., water abounding in calcium salts, soap forms a scum of insoluble salts:



Part of the soap is hydrolyzed by the water:



This is confirmed by the appearance of a crimson coloration when an alcoholic solution of soap, containing a few drops of phenolphthalein, is diluted with water.

106. Soaps and Detergents. Ordinary soap is made by saponifying fats, i.e., the glycerides of the higher (C_{16} — C_{18}) fatty acids. Tallow is heated with a sodium hydroxide solution. When the process of hydrolysis, i.e., the formation of free glycerol and sodium salts of fatty acids, is over, sodium chloride is added to the mixture to salt out these salts; this causes two layers to appear. To make grained soap the sodium salt layer is separated from the lye (from which glycerol is obtained), cooled, turned into shavings, and dried. After colouring materials and perfumes have been crutched in, the soap shavings are compressed and cut into bars of household and toilet soap.

If more concentrated alkali solutions are used for saponification and salting out is omitted, the whole mass solidifies upon cooling. Such soap contains all the glycerol and other admixtures that come from the fat. Soda and sodium silicate are added to laundry soap to make it more alkaline.

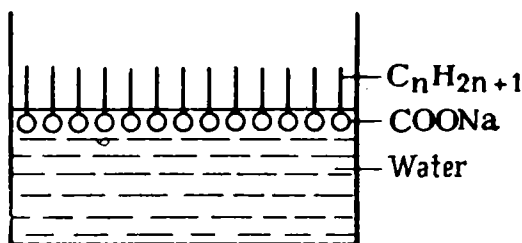
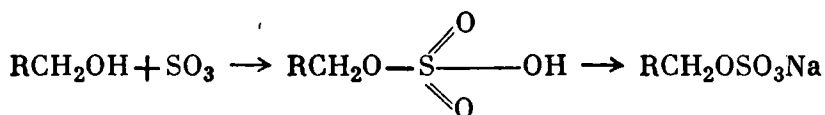


Fig. 36. Orientation of soap molecules on the surface of water.

The cleansing action of soap is based on complicated physico-chemical—or, to be more exact, colloidal—processes and is discussed in greater detail in courses of physical chemistry. Here we shall confine ourselves to a general explanation. Soaps are surface-active substances: their addition to water lowers its surface tension drastically. This can be illustrated by the following simple experiment. Let us pour some pure water into a broad vessel and cover its entire surface with talcum powder or powdered sulphur, i.e., substances which are not wetted by water. If we now introduce a drop of soap solution into the middle of the vessel, we observe an instant rupture of the surface film supporting the powder, a film formed by the surface molecules of the water. Each soap molecule consists of two parts: a big hydrocarbon chain, which is hydrophobic, i.e., is repelled by water, and a carboxyl, or salt, group, which is hydrophilic, i.e., is attracted by water. The soap molecules are oriented on the surface of the water as a layer in such a way that they all float on the water in the form of a palisade (Fig. 36).

Since the mutual attraction between the hydrocarbon parts of the molecules is much weaker than between the water molecules, the firm surface of the film of water is ruptured, and the talcum powder enables us to observe this.

When linen is in contact with our skin, it captures the particles of oil secreted by our sebaceous glands. Greasy linen retains more dust. The globules of oil are not wetted by water and for this reason are not washed away by pure water. But when the linen is washed with soap, the hydrocarbon parts of the soap molecules are turned towards the oil globules, while the hydrophilic carboxyls are turned towards the water phase. The globules are now wetted by the water and emulsified, together with the dirt particles clinging to them; in this form they are easily removed from the fabric. This, of course, is but a primitive description of the mechanism whereby soap exerts its cleansing action. Nevertheless, it suggests ways of seeking substitutes for soap, i.e., substances which have a cleansing action, but are not made from food products (fats and oils) and are free from some of the shortcomings of soap (inhibition of cleansing action in hard or salt water). The following is one of the ways of preparing detergents. If a monohydroxy alcohol $C_nH_{2n+1}CH_2OH$ (where $n = 12, 13, \dots 20$) is by corresponding treatment converted into an acid sulphate



a molecule is formed consisting, like an ordinary soap molecule, of a hydrophobic radical and a hydrophilic group. An advantage of such soaps is that they do not form precipitates with calcium and magnesium salts and, thanks to their higher solubility, can be used in brine and hard water.

The sulphates of the higher fatty alcohols rank among the best synthetic detergents and have extensive industrial and household uses. The initial fatty alcohols are produced from blubber, coconut or tall oil. The synthetic methods are based on the direct oxidation of paraffin hydrocarbons, the reduction of the fatty acids produced by the oxidation of the paraffin, on the oxo synthesis technique, or preparation from lower olefine hydrocarbons with the help of organoaluminium catalysts. The latter method has the advantage that it makes it possible to produce alcohols with a normal chain, which enhances detergent action.

Another important group of synthetic detergents belong to the class of *alkylarylsulphonates*, which have an aliphatic chain and a sulphonated aromatic nucleus.

The already mentioned alkylsulphonates (p. 173) are also of some importance in the production of detergents.

It should be borne in mind that modern high-quality detergents are rather complicated compositions. Usually they contain 20-25% of the surface-active substance (alkylarylsulphonates, alkylsulphates, etc.), up to 50% of phosphates (for example, trisodium polyphos-

phate), various fillers, and 2-3% of activating additives, in most cases carboxymethyl cellulose (p. 323). Such detergents are not only completely satisfactory substitutes for soap, but are superior to it in cleansing action and insensitivity to hard water. They also do not weaken fabrics and irritate the skin less. Progress in methods of synthesizing surface-active substances and using them has considerably reduced soap production in many countries, while the production of synthetic detergents has increased severalfold.

Soaps, it should be remembered, are used in everyday life and in industry not only for washing. They are also good disinfectants, especially when substances such as phenols are added to them.

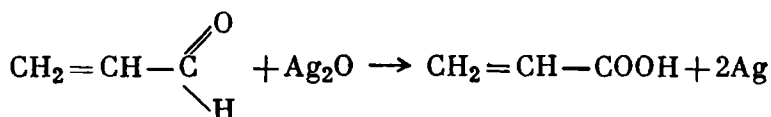
In combating agricultural pests by spraying chemicals, it is often necessary to prepare stable emulsions that would wet the surface of leaves, which are somewhat waxy. For this purpose soaps are added to them.

The salts of the higher fatty acids react with liquid hydrocarbons to form products of a thick consistency. Some of them, such as those based on calcium soaps, are used as lubricating grease (solid oil, etc.).

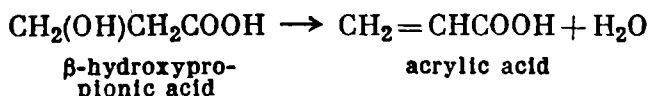
UNSATURATED MONOCARBOXYLIC ACIDS

107. Homologous Series of Unsaturated Monocarboxylic Acids. The composition of an unsaturated monocarboxylic acid molecule with one double bond can be expressed by the general formula $C_nH_{2n-1}COOH$. As acids, these compounds form salts; as unsaturated compounds, they are capable of adding two hydrogen or halogen atoms and undergoing oxidation at the site of the double bond. Vigorous oxidation causes the molecules of these acids to break up. The α,β -unsaturated acids are somewhat stronger than the corresponding fatty acids, since the double bond next to the carboxyl makes its acid properties more pronounced.

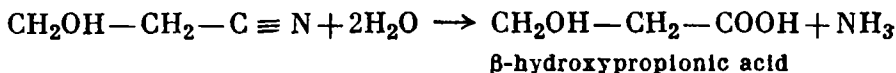
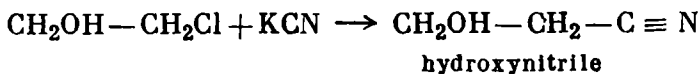
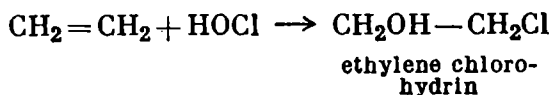
108. Acrylic, Methacrylic, and Crotonic Acids. The simplest unsaturated monoacid, acrylic acid $CH_2=CH-COOH$, can be prepared by oxidizing acrolein by silver oxide:



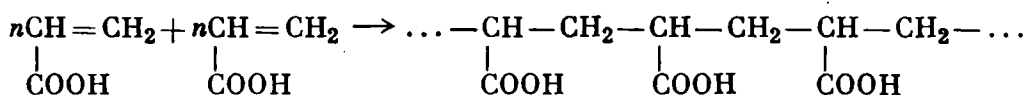
as well as by oxidizing allyl alcohol or saponifying acrylonitrile. Industrially it is prepared by eliminating water from β -hydroxypropionic acid:



Beta-hydroxypropionic acid, in turn, is prepared from ethylene:

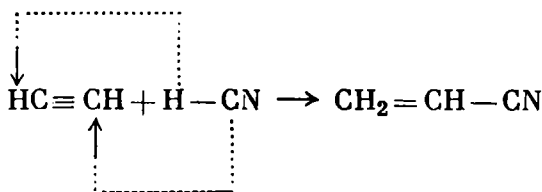


Acrylic acid (m.p. 13° ; b.p. 140°) polymerizes readily to form high-molecular polyacrylic acid:



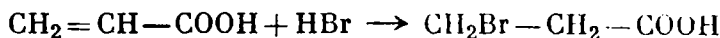
The polyesters of acrylic acid are used as plastics.

Acrylonitrile is a liquid (b.p. 78°) obtained by dehydrating hydroxynitrile (as above) or by adding hydrogen cyanide to acetylene in the presence of catalysts:



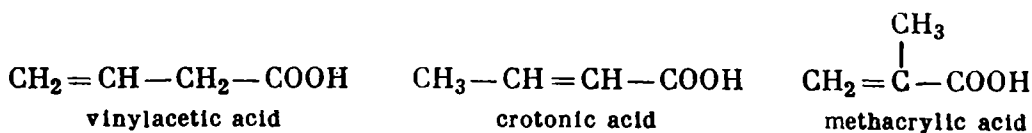
Acrylonitrile is manufactured by the chemical industry in large quantities because it is one of the starting materials in producing synthetic rubber and the fabric *nitron* (*orlon* in the U.S.A.). A co-polymerized mixture of acrylonitrile and butadiene gives a valuable type of synthetic rubber insoluble in petrol.

Acrylic and other α,β -unsaturated acids can add hydrogen halides to form β -halogenated carboxylic acids:



Addition here does not obey Markovnikov's rule (p. 78).

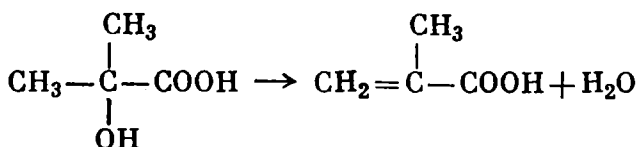
In accordance with the theory of chemical structure, three isomers are possible for the open-chain acids of $\text{C}_3\text{H}_5\text{COOH}$ composition:



They may be regarded as compounds derived by detaching two hydrogen atoms from two neighbouring carbon atoms of butyric acid.

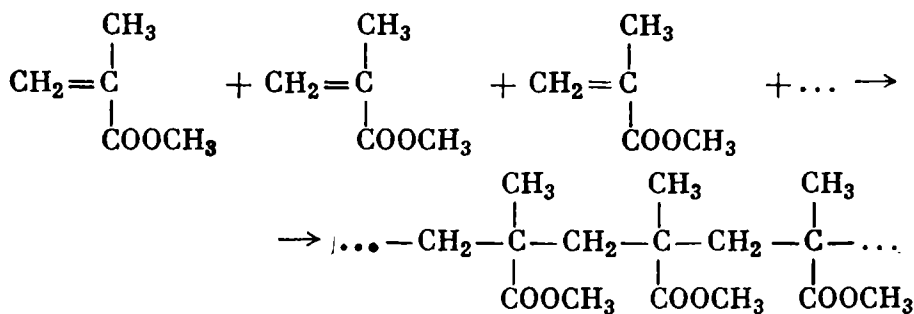
Vinylacetic and crotonic acids are derived in this way from normal butyric acid; methacrylic acid, from isobutyric acid. Methacrylic acid alone has practical importance among these acids, but crotonic acid is the most interesting theoretically.

Methacrylic acid (m.p. 16°; b. p. 160-161°) is prepared by eliminating water from α -hydroxyisobutyric acid (which in turn is prepared from acetone, see p. 262):



The high-molecular esters of methacrylic acid (e.g., the methyl ester) are used to make transparent glass-like plastics, the organic glass plexiglass.

The process of polymerization may be represented as follows:



The dry distillation of the acrylic and methacrylic acid polymeric esters causes the reverse process of depolymerization to take place with the formation of the initial monomers.

Crotonic acid $\text{CH}_3-\text{CH}=\text{CH}-\text{COOH}$ is known in two isomeric forms: crotonic acid (m.p. 72°; b.p. 189°) and liquid isocrotonic acid (m.p. 15.5°; b.p. 172°). On careful oxidation, their molecules break up to form oxalic acid $\text{HOOC}-\text{COOH}$ and acetic acid; on adding hydrogen, each yields butyric acid. The isomerism of these acids is due to the different spatial arrangement of the atoms in their molecules.

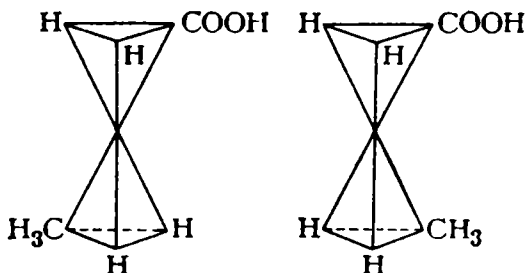


Fig. 37. Spatial configuration of atoms in butyric acid molecule.

109. Cis-Trans Isomerism. If we represent the spatial configuration of the atoms in a molecule of butyric acid by means of two tetrahedra, we obtain the model shown in Fig. 37. In this model there

are carbon atoms of CH_2 methylene groups in the centres of both tetrahedra. If we rotate one of the tetrahedra about the line connecting their centres, we can obtain any number of spatial positions of the atoms of one tetrahedron with relation to the atoms of the other. Two such positions are depicted in Fig. 37.

Isomerism would thus seem to be possible in the case of butyric acid.

However, neither normal butyric acid nor any of the similarly constituted compounds exhibit such "rotation" isomers. This is easily accounted for if we accept van't Hoff's principle of the free rotation of atoms about a single bond.

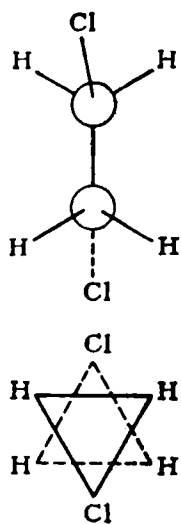


Fig. 38. Rotation isomerism of dichloroethane.

It should not, however, be thought that such rotation is indeed absolutely free. Let us consider, for example, a molecule of dichloroethane (Fig. 38). The C—C atoms, linked by a single bond, are connected with hydrogen and chlorine atoms, which, when rotated about the C—C line, experience mutual attraction or repulsion to a lesser or greater degree. As a result of this, the molecule assumes a certain "conforming" spatial configuration, which in these conditions is the most stable, such as the configuration in Fig. 38, where the identical atoms are as far apart as possible. The existence of such "frozen rotation" has been proved by optical and other physical methods, especially in studying the behaviour of substances at low temperatures.

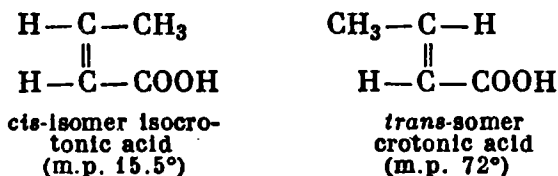
There are also, however, many instances on record of rotation about a single bond being altogether impossible; owing to the interference of neighbouring big atoms and groups. In such cases, e.g., in the derivatives of diphenyl $\text{C}_6\text{H}_5 - \text{C}_6\text{H}_5$, stable rotation isomers have been isolated.

The picture is completely different if the two carbon atoms are doubly bound.

Let us consider the case of crotonic acid as an example.

To obtain a molecule of crotonic acid we must remove two hydrogen atoms from a molecule of butyric acid; the valency units thus freed saturate each other. In terms of the tetrahedral model this is depicted by combining two tetrahedra edgewise (Fig. 39). Such a configuration of atoms renders free rotation impossible, since this would involve bond rupture. The hydrogen atoms of the crotonic acid molecules may be either on the same or on different sides of the plane passing through the carbon atoms and the double bond. The former position is designated by the prefix *cis* before the name of the isomer; the latter configuration, by the prefix *trans*.

The crotonic acid *cis*- and *trans*-isomers may be represented schematically as follows:



Another example of *cis-trans* isomerism is provided by oleic and elaidic acids (p. 232).

The theory of this type of isomerism was evolved in 1887 by J. Wislicenus on the basis of van't Hoff's tetrahedral model.

The study of the chemical properties of the two isomers makes it possible to choose a definite configuration for each (p. 258 fol.).

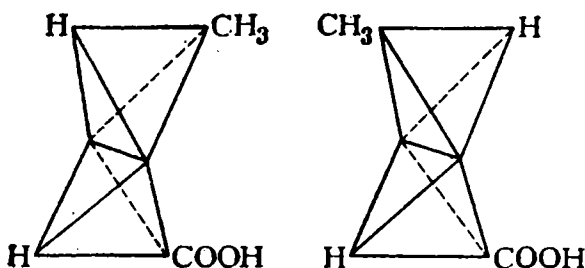
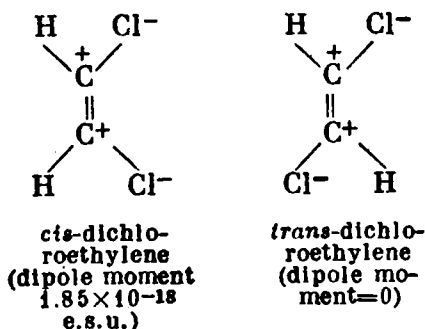


Fig. 39. Crotonic acid stereoisomerism.

Cis- or *trans*-configuration can in many cases also be determined from dipole moments.

Cis-isomers of the 1,2-dihalogen derivatives of ethylene must have a dipole moment; the *trans*-isomers (with the same number of halogen atoms) cannot have a dipole moment because of the internal compensation of the positive and negative charges:



The relationship between the *cis-trans* isomers of the unsaturated acids is an extremely interesting one. One of the isomers (e.g., cro-

tonic or elaidic acid) is more stable than the other (isocrotonic or oleic acid). The unstable isomer (labile form) upon heating or under the action of certain substances (H_2SO_4 , KOH , HNO_3) turns into the stable. The transformation is speeded by the presence of bromine or iodine traces and direct sunlight. The reverse transformation takes place under the action of ultraviolet rays or can be effected by means of several chemical reactions.

110. Strain Theory. The valency units of a carbon atom are directed from the centre towards the vortices of a tetrahedron and form angles of $109^\circ 28'$. Baeyer made the assumption that when a double bond

is formed, there is a deviation of the valency units to the line connecting the atom centres. Accordingly, to find the directions of the valency units, say, of an ethylene molecule, we must fold the drawing (Fig. 40) until the original directions of the valency units intersect and then halve the angles between them. Since this angle is $109^\circ 28'$, the deviation of the valency units when a double bond is formed between the carbon atoms is equal to

$$\frac{109^\circ 28'}{2} = 54^\circ 44'$$

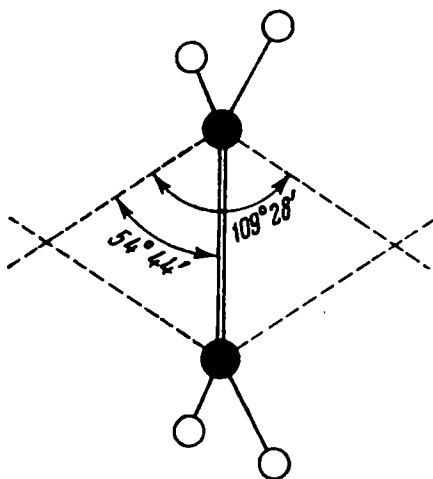


Fig. 40. Deviation of valency units when a double bond is formed between carbon atoms.

Such a position of the valency units is less stable, and they seek to resume their former stable tetrahedral configuration. This tendency is termed *strain*

In other words, the theory of strain postulates essentially that *the most stable configuration of atoms in molecules of organic compounds is the tetrahedral configuration*. Any other configuration is less stable and tends to revert to the tetrahedral.

The theory of strain was advanced by Baeyer in 1885. It provided the possibility of uniting, interpreting, and predicting a large number of highly important phenomena. It is, however, easily given a wrong, purely mechanical interpretation. When applying the theory, it should therefore always be borne in mind that chemical forces differ qualitatively from the mechanical forces by which the Baeyer theory is represented in models.

111. Electronic Structure of Double Bonds (π -Bonds). As was stated earlier, the structure of ordinary homoeopolar bonds is best interpreted in terms of electronic notions. A single bond is a so-called σ -bond, with its characteristic electron clouds. Such a bond is distinguished by: a) relative chemical inertness; b) free rotation; c) definite

values of interatomic distances (about 1.52-1.54 Ångström units), and d) definite values of intervalency angles (about 110°).

Classic organic chemistry operated with constant mechanical models of bonds, without probing deeper into the nature of the chemical bond.

The unsaturated carbon-carbon bond was pictured as a system of two atoms linked by identical valencies. To account for the existence of *cis-trans* isomers on the basis of this concept, approximate tetrahedral models were introduced. The explanation of characteristic reactivity involved the assumption of a peculiar "splitting" of valencies, with the appearance of "additional", or "partial", valencies. With the birth of the first electronic concept, in accordance with which the

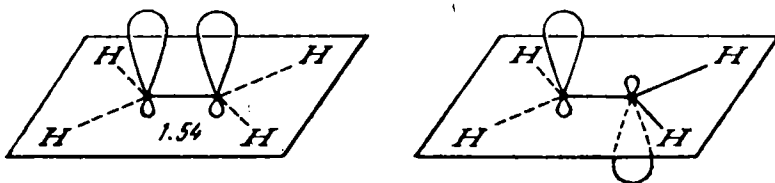


Fig. 41. Electronic structure of the ethane molecule residue after the removal of two hydrogen atoms.

double bond was represented as four common electrons rather than two identical lines, it became possible to propose electronic models of the double bond.

Modern physics enables us to form a clearer picture of multiple bonds and to account for the characteristic properties of unsaturated compounds.

Let us assume that the methyl radicals in the ethane molecule have each lost a hydrogen atom (Fig. 41). This should give rise to two "free" linkages. Evidently, this must involve a drastic change in the movement of the electrons responsible for these valencies, as well as in the spatial configuration and chemical character of the molecules.

All six atoms of the ethylene molecule are situated in one plane and are still linked by σ -bonds, which form equal angles with one another ($360:3 = 120^\circ$). The movement of the two "free" electrons is in a direction perpendicular to the plane of the molecule; their electron clouds appear to form symmetric spatial "eights", which are perpendicular to the molecule's plane (Fig. 42).

The linkage effected by such electrons is called a " π -bond".

The presence of a π -bond in a molecule gives it the following distinctive features:

1. It produces additional attraction, which reduces the distance between the carbon atoms from 1.54 to 1.34 Ångström units.

2. It gives rise to additional forces directed perpendicularly to the plane of the molecule, abolishing or hampering rotation about the line connecting the carbon atoms. This makes possible geometric (*cis-trans*) isomers.

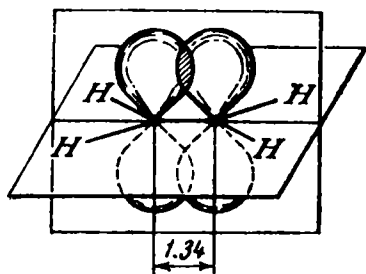


Fig. 42. Electronic structure of ethylene molecule.

3. The linkage of two carbon atoms by the σ - and π -bond system becomes thermodynamically more stable (the double bond being represented by the two lines $C=C$).

Intense heating causes saturated hydrocarbons to give up hydrogen atoms and become olefines.

4. The action of chemical reagents is as a rule directed first and foremost at

the doubly bound carbon atoms. This is due to the specific nature of the electrons effecting the π -bond: they are much more mobile and their electron clouds are more easily displaced by external influences.

Let us consider, for example, the addition of HBr to ethylene. The study of such processes has shown that the reaction begins with the action of the more active H^+ proton. When it approaches one of the carbon atoms, it causes a rearrangement of the mobile electron clouds of the π -bond in such a manner that the electronegative character of this carbon atom becomes more pronounced, while the electronegative character of the neighbouring C atom becomes less pronounced (Fig. 43a, b).

The next stage is the addition of the Br^- ion to the neighbouring C atom (Fig. 43c).

In the case of ethylene or other symmetric olefines both carbon atoms are identical, and the π -bond electron clouds are likewise symmetric. The addition of HBr to dissymmetric olefines obeys Markovnikov's rule, and the hydrogen is added to the more hydrogenated carbon atom.

Isobutylene provides an example of this. It has a dipole moment of $0.49D$.

The positive end of the molecule is naturally on the side where there are more hydrogen atoms (Fig. 44). That means that the electron clouds forming the π -bond are displaced to the right.

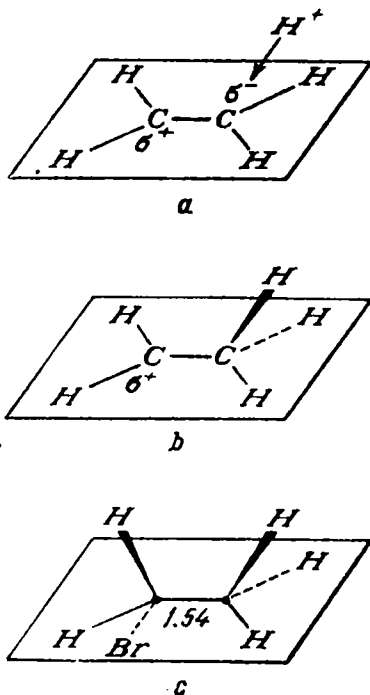


Fig. 43. Addition of HBr to ethylene:

a—proton approaches carbon atom; b—proton is added; c— Br^- ion is added to neighbouring carbon atom.

It is therefore clear that the consecutive addition of an H^+ ion and then a Br^- ion will give rise to 2-bromo-2-methylpropane (Fig. 45). The addition of $H(SO_4H)$ and $Cl(OH)$ proceeds similarly.

The action of oxidizing agents (say, $KMnO_4$ or ozone) is also directed primarily at the double bond. The result is a saturated compound (e.g., a dihydroxy alcohol or ozonide). Further oxidation gives rise to the ketone group, with subsequent oxidation according to A. Popov's rule (p. 188) or according to the ozonide disintegration pattern (p. 79). As a result, the molecule is ruptured at the double bond. All this shows that the double bond is the "weak spot" of a molecule with respect to chemical action.

5. A double bond not only links the carbon atoms more firmly, but also reduces the mobility of other atoms (H , Cl) attached to these carbon atoms (p. 111)

We have established that the double bond consists of a σ -bond and a π -bond. Therefore, when a chemist represents the double bond by

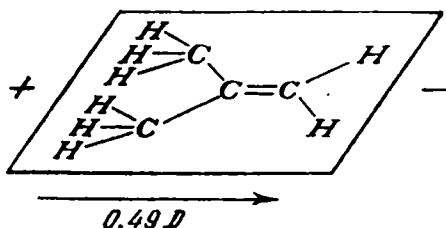


Fig. 44. Structure of isobutylene molecule.

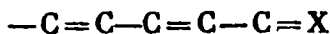


Fig. 45. Addition of HBr to isobutylene molecule.

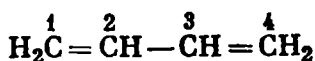
the traditional two identical lines, he must bear in mind the present day concepts for which that symbol stands.

As for the causes of "strain" in the double bond (p. 226), they are nowadays referred to simply as representing a historical stage in the efforts to explain these phenomena.

112. Conjugated Double Bonds (Conjugates). Electronic notions have made it possible to account for a number of distinctive features of compounds containing several double (or, in the general case, multiple) bonds that form a conjugated pattern



Let us consider the simplest example of this, divinyl:



The molecule of this compound contains four consecutive carbon atoms, the σ -bonds alternating with σ - and π -bonds (Fig. 46).

The mutual influence of the electron clouds greatly affects the linkage between the second carbon atom and the third. Investigations have revealed that this is no longer an ordinary σ -bond with an interatomic distance of 1.54 Ångström units; in divinyl and its homologues and analogues the distance between the second atom and the third equals 1.46 Ångström units. Moreover, all the atoms of divinyl lie in one plane.

The new electronic notions account much more fully for the characteristic chemical properties of compounds with conjugated multiple

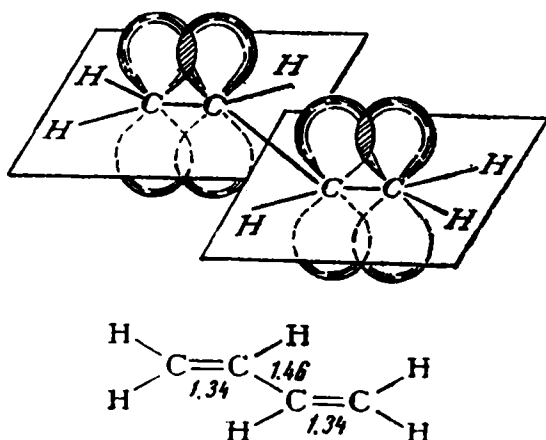
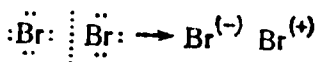


Fig. 46. Structure of divinyl.

bonds than did the hypothesis of partial valencies (p. 94). This applies above all to addition reactions. Thiele's theory could explain 1,4-addition, but failed to account for 1,2-addition, which is quite frequent.

Let us consider, for instance, the addition of a bromine molecule to divinyl.

As stated earlier (p. 55), halogenation commences with the break-up of the halogen molecule:

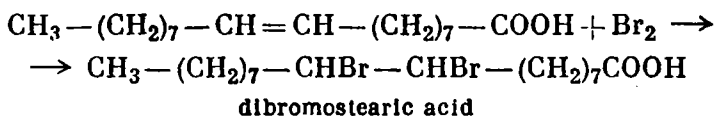


The bromine atom with the positive charge, on approaching one of the extreme carbon atoms, causes an increase of the electron density there, with a simultaneous polarization of the entire molecule (the arrow indicates the electron density shift):



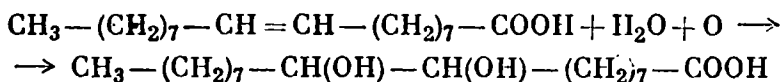
The acid is a colourless oily liquid, which is lighter than water and solidifies in the cold into needle-like crystals melting at 14° . When exposed to the air, it quickly undergoes oxidation, acquiring a yellow colour.

The molecule of oleic acid is capable of adding two halogen atoms:

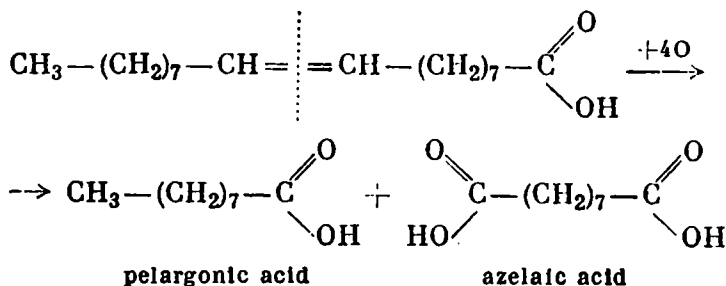


In the presence of catalysts it adds two hydrogen atoms, forming stearic acid.

When oleic acid is oxidized by an alkaline potassium permanganate solution, the hydroxyls are added to the doubly bound carbon atoms:



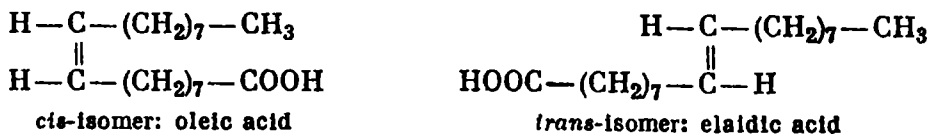
More vigorous oxidation splits the molecule:



The oxidation of oleic acid with the formation of two acids, pelargonic and azelaic, whose molecules contain normal chains of nine carbon atoms, proves the structure of oleic acid, i.e., the presence in its molecule of a normal carbon chain and the position of the double bond between the ninth carbon atom and the tenth.

When oleic acid is treated with a small quantity of nitric acid, it solidifies into its isomer, elaidic acid.

The isomerism of oleic and elaidic acids is an instance of *cis-trans* isomerism:



Oleic acid is obtained as a by-product at stearin factories; it is used in soap-making, adhesive plaster manufacture, and in wool oiling before spinning.

Linoleic acid $\text{C}_{17}\text{H}_{31}\text{COOH}$ and linolenic acid $\text{C}_{17}\text{H}_{29}\text{COOH}$ are even more unsaturated than oleic acid. The glycerides of these acids

are the main components of linseed and hempseed oils. The linoleic acid molecule contains two double bonds and is capable of adding four hydrogen or halogen atoms. The linolenic acid molecule contains three double bonds and can therefore add six hydrogen or halogen atoms. On adding hydrogen, both form stearic acid.

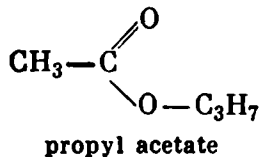
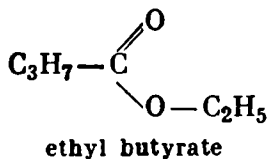
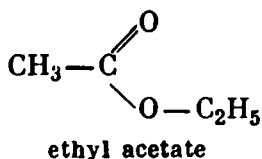
114. Plastics Based on Polymers of Acrylic and Methacrylic Acid Derivatives. Acrylic acid, as well as methacrylic acid, readily undergoes polymerization at temperatures below 100° in the presence of organic or inorganic peroxides and oxygen. The polymers of both acids and of their derivatives (esters, nitriles, amides, see p. 223) are termed *polyacrylates*. This is a vast and varied class of polymeric plastics, which has become very important in technology. The plastics based on the acrylic acid polymers are colourless, have a stability to light and optical clarity. Some of them are hard, resilient glass; others are soft, rubber-like, and even wax-like substances.

Polyacrylic glass has many technical and household uses. A valuable technical property of the polyacrylates is their ability to transmit ultraviolet rays. For example, polymethylmethacrylate transmits over 99% of sunlight and is in this respect far superior to lime-silicate glasses. The superiority of polyacrylate glasses is borne out even more strikingly by a comparison of their ability to transmit the ultraviolet part of the spectrum; for instance, quartz glass transmits 100% of ultraviolet rays, polymethylmethacrylate glass 73.5%, plate glass 3%, and ordinary lime-silicate glass 0.6%. Polyacrylates, moreover, have other valuable properties: organic glass is ten times stronger than mineral glass and lends itself well to mechanical treatment.

Acrylic water emulsions (of the latex type) are becoming important for impregnating fabrics, wood, paper, treating leather, etc. They have found application in the production of medical adhesives, uncreasable fabrics, and as ingredients in the making of imitation leather. They are also used as protective varnishes for metal and wood, as well as in building work to make concrete waterproof, as grounding in interior decoration, to impregnate porous building materials, etc.

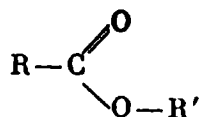
ESTERS OF CARBOXYLIC ACIDS

115. Structure and Preparation of Esters. From the structural formulas of the carboxylic acid esters



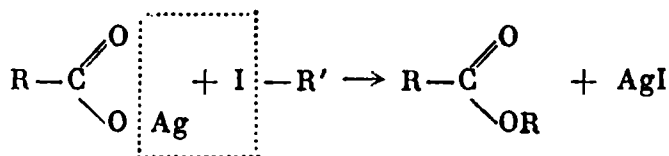
it is evident that *the carboxylic acid esters may be regarded as the products of the substitution of a hydrocarbon radical for the carboxyl hydrogen.*

The general formula of the esters is therefore:

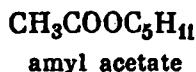
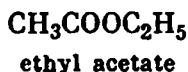
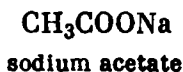


where R and R' are hydrocarbon radicals.

The structure of the esters is established by their preparation by the action of alkyl halides on salts:

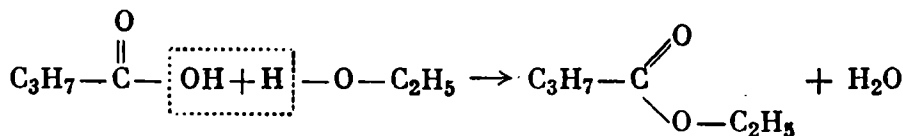


The names of the esters are composed like the names of salts: the salts of acetic acid being acetates, the corresponding ethyl ester is called ethyl acetate, the amyl ester, amyl acetate, etc.

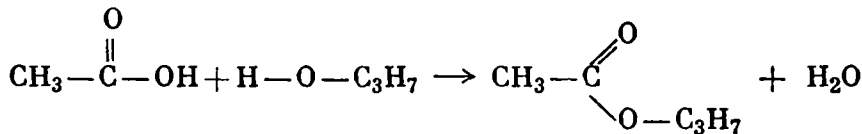


116. Esterification. Many esters are easily prepared by the direct interaction of a carboxylic acid and an alcohol in the presence of sulphuric acid. This reaction is called *esterification*.

For instance, when sulphuric acid acts upon a heated mixture of butyric acid and ethyl alcohol, we obtain ethyl butyrate:



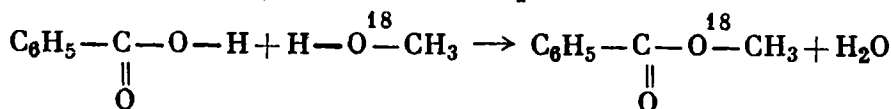
From acetic acid and propyl alcohol we obtain propyl acetate:



In this reaction a hydrogen atom is removed from the hydroxyl group of the alcohol, while a hydroxyl is removed from the acid molecule.

This pattern of the reaction, considered highly probable in the past, has now been confirmed experimentally. Urey (1938) treated benzoic acid $\text{C}_6\text{H}_5\text{COOH}$ (in the presence of a small quantity of hydrogen chloride) with methyl alcohol containing a certain amount

of the oxygen isotope O^{18} . The resulting water contained no heavy oxygen. Consequently, the reaction proceeded as follows:



i.e., the hydroxyl comes from the acid molecule and not from the alcohol molecule.

Fig. 47 shows a laboratory arrangement for preparing ethyl acetate. A mixture of 50 ml of ethyl alcohol and 50 ml of concentrated

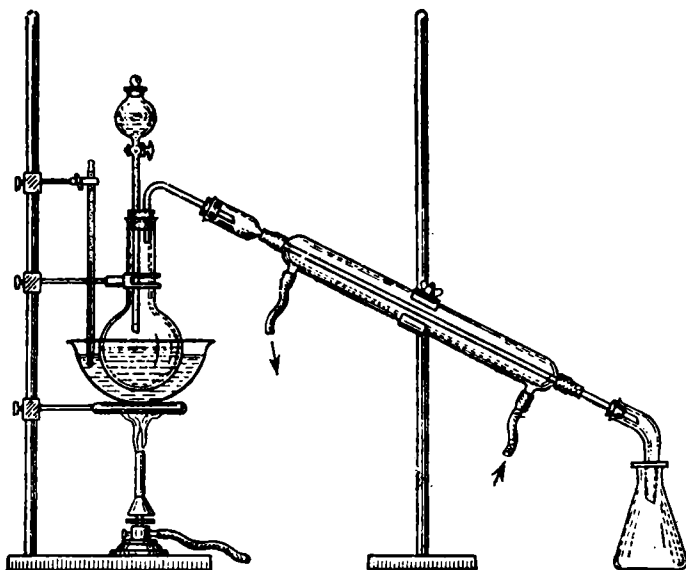


Fig. 47. Laboratory arrangement for preparing ethyl acetate.

sulphuric acid is poured into a flask, which is placed in an oil bath for temperature regulation. When the mixture has been heated to 140° , 400 ml of a mixture of equal volumes of alcohol and acetic acid are added slowly. The resulting ester and water are distilled into the reservoir. To remove admixtures of the acid the mixture is shaken with a soda solution, while to remove alcohol admixtures it is shaken with a calcium chloride solution. The ester is then separated from the water in a separating funnel (it is lighter than water and immiscible with it), dried by means of calcium chloride, and redistilled. This generally practised method of preparing ethyl acetate was proposed in 1873 by Markovnikov, who also explained the mechanism of the reaction.

Esterification is a reversible reaction: it does not proceed to the end, since parallel with it there takes place the reverse reaction of hydrolysis (*saponification*), i.e., the break-up of the ester into an acid and an alcohol.

Equilibrium, which is practically unaffected by temperature, depends substantially upon the nature and quantity of the acid and the alcohol. In the case of ethyl alcohol and acetic acid, taken in equimolar quantities, equilibrium sets in when two-thirds of the alcohol and acid have been turned into the ester.

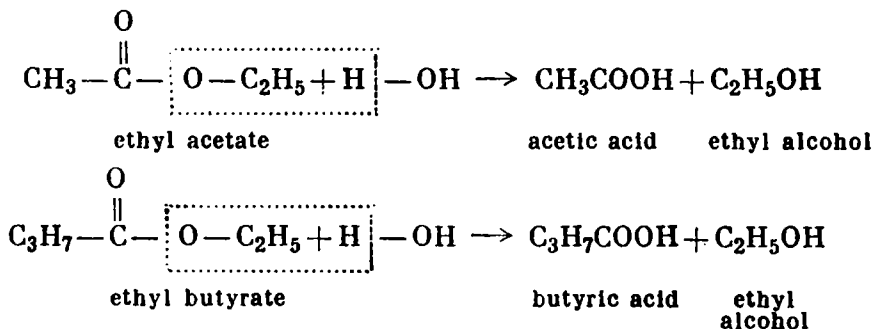
By applying the law of mass action, we see at once that the addition of sulphuric acid, which binds the water, raises the esterification limit considerably. Similarly, by taking in excess one of the reactants, i.e., the acid or the alcohol, we can secure the almost complete esterification of the other reactant.

N. Menshutkin demonstrated that the rate of ester formation differs for primary, secondary, and tertiary alcohols. As a rule, primary alcohols form organic acid esters more rapidly than do secondary alcohols, while they act faster than do tertiary alcohols. When, for instance, different alcohols are heated with an equivalent amount of acetic acid for one hour to 155°, primary alcohols are found to have been esterified to the extent of 46-47%; secondary alcohols, not more than 22%, and tertiary alcohols, approximately 2% (Menshutkin's data).

The preparation of esters from acid chlorides and anhydrides is discussed on p. 247; the preparation of esters from aldehydes by the Tishchenko reaction, on p. 186.

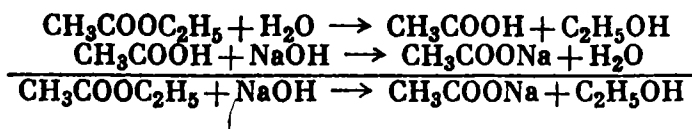
117. Properties of Esters. The lowest representatives of the esters are volatile liquids with a low solubility in water. Many esters have very pleasant odours, some of which resemble fruit odours.

1. Hydrolysis (Saponification) of Esters. The fact that the acid and alcohol residues are linked through oxygen atoms in esters is a distinctive feature responsible for many of their properties. Whereas the carbon chain of an ester is very difficult to rupture, the linkage via oxygen is usually easily broken even by the action of water (hydrolysis):



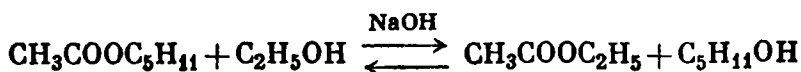
The hydrolysis of an ester to an alcohol and an acid by the action of water proceeds slowly, but the addition of a small amount of inorganic acid speeds the reaction considerably. The acid undergoes no change, merely accelerating the reaction catalytically. Alkalis

similarly accelerate saponification, but in this case the reaction is somewhat more complex. The alkali not only accelerates the reaction (the OH ions act as a catalyst), but also reacts with the acid formed to produce a salt and an alcohol:



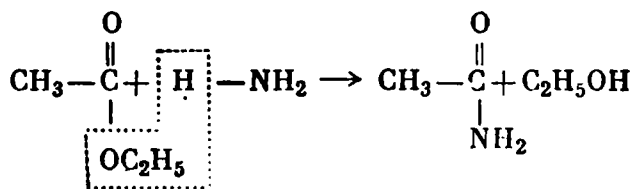
The presence of an alkali therefore makes the reaction of hydrolysis irreversible.

2. *Alcoholysis of Esters.* The heating of an ester in an alcoholic solution can bring about an exchange of alcoholic radicals:

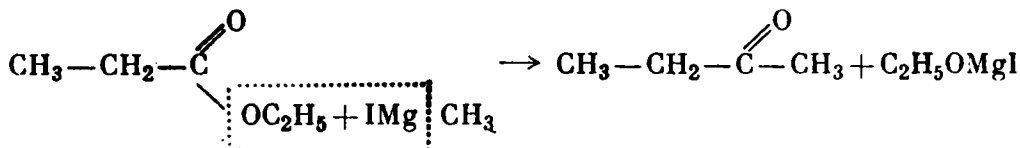


The reaction is usually conducted in the presence of an alkali; a complete exchange of alcoholic radicals can be effected if the alcohol is taken in excess and the resulting ester (which is more volatile) is distilled off. This is the procedure for preparing fatty acid esters from fats.

3. *Ammonolysis of Esters.* The action of ammonia, even at a low temperature, often splits esters, with the formation of acid amides:

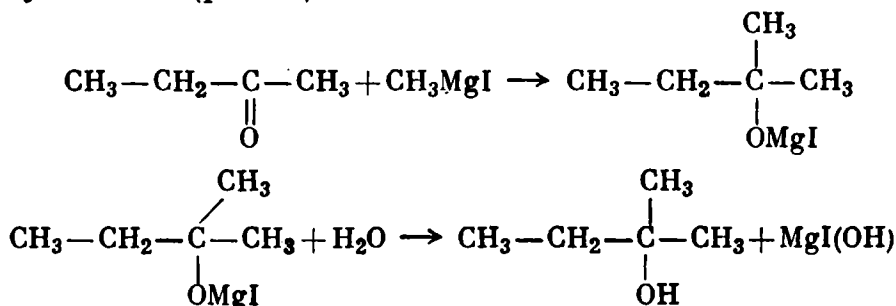


4. *The action of organomagnesium compounds on esters produces ketones and tertiary alcohols:*

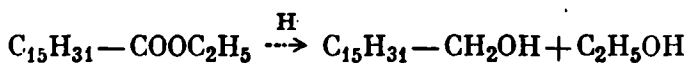


The reaction can be halted at the stage of ketone formation if it is conducted with an insufficient amount of the organomagnesium compound and the temperature is kept very low. Otherwise the ketone reacts with more of the organomagnesium compound to form a

tertiary alcohol (p. 182):



5. The reduction of esters produces primary alcohols with the same number of carbon atoms as there are in the acid from which the ester comes:



The reaction is brought about by the action of metallic sodium on an alcoholic (ethyl or butyl) solution of the ester. Lately the preferred reducing agent has been gaseous hydrogen under pressure in the presence of a so-called *skeleton nickel catalyst* (prepared from a nickel-aluminium alloy by treatment with a sodium hydroxide solution and known as the *Raney catalyst*).

118. Some Representative Esters of Carboxylic Acids. Many esters, as mentioned above, have pleasant fruity odours.

Formic Acid Esters. Ethyl formate $\text{H}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OC}_2\text{H}_5 \end{array}$ boils at 55° and has an odour of rum.

Acetic Acid Esters. Ethyl acetate is a liquid with a refreshing odour; it boils at 77° and is but slightly soluble in water. Ethyl acetate has many uses as a reagent and a solvent. As stated above, it can be prepared from acetaldehyde by the action of aluminium alcohols (Tishchenko reaction).

Isoamyl acetate $\text{CH}_3-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OC}_5\text{H}_{11} \end{array}$ boils at 139° and has an odour of pears. It is used in large quantities as a solvent in the manufacture of lacquers.

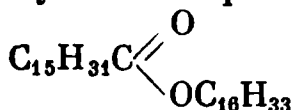
Butyric Acid Esters. Ethyl butyrate $\text{C}_3\text{H}_7-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OC}_2\text{H}_5 \end{array}$ boils at 121° and has an odour of apricots. Butyl butyrate $\text{C}_3\text{H}_7-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OC}_4\text{H}_9 \end{array}$ has an odour of pineapples.

Isoamyl isovalerate has an apple-like odour.

The above esters are used in the manufacture of artificial fruit essences, which are very much in demand in the production of confectionery, perfumery, and non-alcoholic beverages.

119. Waxes. Waxes consist primarily of esters of the higher fatty acids and high-molecular monohydroxy alcohols. They may also contain high-molecular alcohols and acids in the free state, as well as some of the higher hydrocarbons. Beeswax consists for the most part of myricyl palmitate $C_{15}H_{31}COOC_{30}H_{61}$; it also contains 10-14% of cerotic acid $C_{25}H_{51}COOH$ and 12-17% of hydrocarbons.

Spermaceti is a solid derived from the oily liquid in the head cavity of the sperm whale; it consists mainly of cetyl palmitate



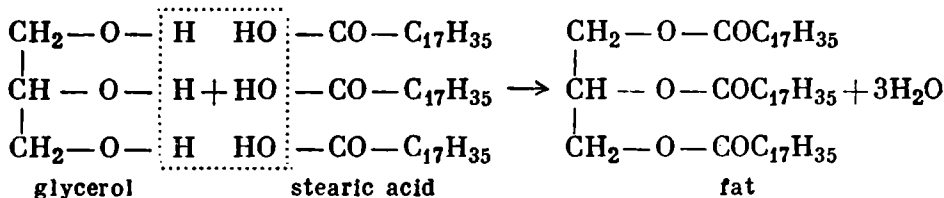
120. Fats. Fats occur widely both in animal organisms and in plants. As pointed out above, they are esters of the trihydroxy alcohol glycerol and various acids, mainly stearic, palmitic, oleic, linoleic, and linolenic. This is confirmed by their break-up into glycerol and acids, and by the subsequent synthesis of fats from these products.

The structure of fats was established in the early 19th century by Chevreul. On treating animal and vegetable fats with an alkali, he observed that the weight of the saponification products exceeds the weight of the initial fat by about 5%. The weight of the carbon in this case remains the same, whereas the amounts of oxygen and hydrogen increase in the proportion in which these elements are contained in water. From this he drew the conclusion that the saponification of fats involves the addition of water.

Chevreul obtained three acids from the disintegration of fats: the two solid stearic and margaric acids and the liquid oleic acid.

In some fats (e.g., in butter and in castor-oil) Chevreul discovered other acids in addition to these three: in this way he discovered butyric, caproic, and capric acids. Chevreul's margaric acid later turned out to be a mixture of stearic acid and palmitic acid (the latter was discovered in the middle of the 19th century).

The first synthesis of fats was effected by M. Berthelot (1854), who heated glycerol with acids in sealed tubes:

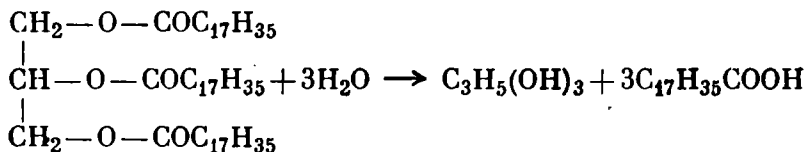


The glyceride of stearic acid is tristearin; the glyceride of palmitic acid, tripalmitin. Tristearin and tripalmitin are solids. Triolein, i.e., the glyceride of oleic acid, is a liquid which solidifies at -4° . The glycerides of linoleic and linolenic acids are likewise liquids.

The first three of these substances in various proportions form the bulk of animal fat. The more tristearin and tripalmitin there is in the fat, the harder it is (beef and mutton tallow). Soft fats (goose fat and lard) contain more triolein.

Fats are of tremendous importance in nutrition. In calorie value they rank highest among the foods: 1 g of fat produces 9.3 Cal. Fats also have important industrial applications: they serve as materials for the production of stearin, soap, and glycerol.

121. Decomposition of Fats. The technical processing of fats consists primarily in their saponification, i.e., their decomposition into glycerol and acids:



This process is usually conducted in the presence of catalysts, such as the oxides of certain metals (lime, magnesia, zinc oxide) or specially prepared organic substances. One of the latter used extensively is the "Petrov contact", which is prepared by the treatment of certain petroleum fractions with sulphuric acid.

The Petrov contact is a thick clear liquid, dark-yellow to brown in colour, with a bluish tint. It usually contains about 40% of naphthene sulphonic acids, 15% of vaseline oil, some free sulphuric acid, and water. Because it emulsifies fats, it increases the interface of the fat and the saponifying liquid, thereby accelerating the reaction.

The decomposition of fats in the animal organism takes place under the influence of a special enzyme, *lipase*. It is secreted by the pancreatic gland and is found in the stomach, in intestinal juice, in the blood, etc.

Under the influence of lipase, fats decompose in the intestines into glycerol and acids, which the organism reconverts into fats.

Lipase occurs in many plants, especially in the beans of the castor-oil plant, which are used for the industrial decomposition of fats. Decomposition is conducted at temperatures of 10 to 40°, the fat being converted into an emulsion.

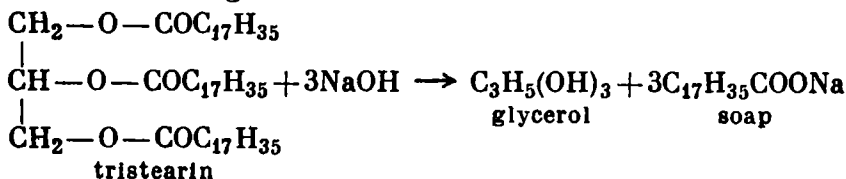
The fat is mixed with a small amount of water and stirred thoroughly by aeration, with the addition of an emulsion prepared from castor-oil beans and a small amount of manganous sulphate (to activate the lipase). After approximately two days the decomposition is practically complete.

Lipase decomposes not only fats, but nearly all esters.

122. Stearin Manufacture and Soap-Making. Stearin is made from solid fats, which, upon saponification with sulphuric acid, yield primarily stearic, palmitic, and oleic acids. The acids, after purifica-

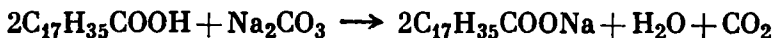
tion by steam distillation, are wrapped in coarse cloth and placed under a hydraulic press. Pressure expels the liquid oleic acid, leaving only the stearic and palmitic acids in the cloth. This mass is called stearin and is used in candle-making. The oleic acid is used in soap-making.

Saponification in soap-making is effected by alkalis. The fats in this case are decomposed into glycerol and soaps, i.e., sodium and potassium salts of high-molecular acids:



Diverse fats are used in soap-making: animal fat, hempseed oil, cottonseed oil, etc. An important material in soap-making is oleic acid, a by-product of stearin manufacture.

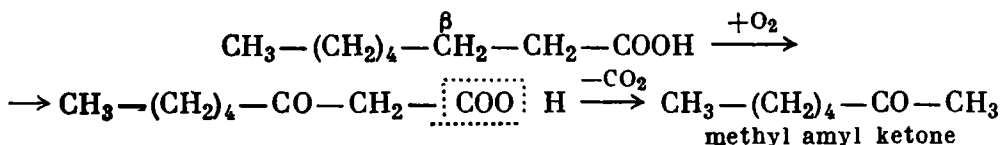
At some factories the soap-making procedure is different. The fat is first decomposed into glycerol and acids, and the acids are then treated with soda:



This procedure makes it possible to obtain very pure glycerol and to use cheap soda as a substitute for expensive sodium hydroxide.

123. Vegetable Oils. Vegetable oils may be either solid or liquid. The solid ones (palm-grease, coconut oil) contain considerable amounts of tristearin and tripalmitin, whereas the liquid oils consist chiefly of the glycerides of unsaturated acids (oleic, linoleic, or linolenic). According to their behaviour when exposed to air, the liquid oils are divided into drying, semi-drying, and non-drying oils.

The non-drying oils (olive oil, almond oil) consist largely of triolein. Storage—and, especially, exposure to light—cause them to become rancid. This is due to the fact that, mainly under the influence of microorganisms, the fat decomposes into glycerol and acids, both saturated and unsaturated. The unsaturated acids undergo oxidation, breaking up into aldehydes and acids with fewer carbon atoms in the molecule. The saturated acids decompose under the influence of microorganisms to form ketones. Some of the ketones, such as methyl heptyl ketone, have an unpleasant rancid odour. The acid decomposition follows the β -oxidation pattern, i.e., the carbon atom in β -position with respect to the carboxyl group experiences the oxidation:



The *drying oils* (linseed oil, hempseed oil) consist primarily of the glycerides of linoleic and linolenic acids. A distinctive feature of these oils is their ability, upon exposure to light and air, especially in thin layers, to dry, forming a solid elastic film. When drying, the oils combine with oxygen; this is attended by a rise in temperature to such an extent that oily rags can ignite spontaneously. The weight of the oil, upon drying, is 11-18% greater. Oxidized and polymerized linseed oil is called *linoxyn*. This is a thick, brownish, elastic substance used in the manufacture of linoleum, Lincrust, and oil-cloth.

Semi-drying oils (sunflower oil, cottonseed oil) differ from drying oils by having a low content of linolenic acid; they differ from non-drying oils by having a relatively high content of linoleic acid.

Table 10 gives the approximate composition of some fats and oils.

TABLE 10. Composition of Some Fats and Oils

Fat or oil	Content, in %			
	Tristearin and tripalmitin	Triolein	Trilinolein	Other glycerides
Beef tallow	75	25	0	0
Butter (with some glyceride of butyric acid)	53	39	0	8
Olive oil	25	70	5	0
Cottonseed oil	25	25	47	3
Sunflower oil	6.5	33	58	2.5
Linseed oil	8	18	30	44
Hempseed oil	0	15	70	15

The degree of unsaturation of a fat or oil is determined by the amount of bromine or iodine absorbed by a known quantity of the substance. In practice it is preferable to use iodine, but since the direct addition of iodine at the double bond is observed very seldom, the reaction is conducted in special conditions: in an alcoholic solution of mercuric chloride. The degree of unsaturation is expressed by what is known as the *iodine number*, i.e., the number of grams of iodine absorbed by 100 g of the fat. The higher this number, the more of unsaturated glycerides there evidently are in the fat or oil.

The iodine numbers of some fats and oils are listed below:

beef tallow	35-40	sunflower oil	129-136
lard	48-64	hempseed oil	145-162
olive oil	77-91	linseed oil	175-201
cottonseed oil	104-116		

Large quantities of drying oils are used to make drying oil, a thick, rapidly drying liquid. To make drying oil, linseed oil is heated in the presence of catalysts called *siccatives*. The manganous, lead, or cobalt salts of certain acids (linseed oil or colophony) are used as catalysts. In accordance with one of the prescriptions for making siccatives, the linseed oil, colophony, or petroleum acids are heated with a certain amount of minium Pb_3O_4 , manganese dioxide MnO_2 , or cobalt acetate $(CH_3COO)_2Co$. Siccatives are ordinarily used in solution in petroleum oils.

The process of making drying oil consists in the polymerization and oxidation of the oil. Sometimes the heated oil is aerated before the siccatives are introduced; the oxygen of the air oxidizes the glycerides.

Drying oil is used to make oil paints and lacquers, and is used in printing. Good drying oil dries within 4-5 hours.

Printers' drying oil is made without siccatives and without access of air in an atmosphere of carbon dioxide.

124. Hydrogenation of Fats. Liquid vegetable oils consist mostly of the glycerides of oleic, linoleic, and linolenic acids. They contain but insignificant amounts of tripalmitin and tristearin.

For a long time chemists sought to convert liquid vegetable oils into solid fats suitable for industrial use and for cooking. This problem was solved at the beginning of this century, and today the conversion of vegetable oils (and seal oil) into solid fats constitutes a whole industry.

The process, which is called hydrogenation of fats, consists in converting the liquid glycerides of unsaturated acids into the solid glycerides of saturated acids through the addition of hydrogen. The hydrogen is easily added under pressure in the presence of certain catalysts (usually finely divided nickel). Hydrogenation is achieved by the passage of the hydrogen through the heated vegetable oil in an autoclave, the catalyst being in suspension (Fig. 48). The product is filtered warm under pressure through cloth to separate the catalyst and is poured into barrels, in which it solidifies into a product called *hardened oil*. The technology of the hydrogenation of fats was first developed by S. Fokin (1865-1917).

Some types of vegetable oils yield excellent edible fats, which are used mixed with vegetable oil and milk (margarine). The mixing is done in special machines, which convert their charge into an emulsion.

125. Synthetic Fatty Acids. Carboxylic acids with 10 to 20 carbon atoms in the chain are produced industrially from paraffin wax to serve as substitutes for edible fats in soap-making. Paraffin wax consists of saturated hydrocarbons of the composition $CH_3-(CH_2)_n-CH_3$, where n ranges from 18 to 38. They are oxidized by air at $100-120^\circ$ in the presence of a catalyst, in most cases

potassium permanganate. In these conditions the carbon chain is ruptured and the CH_3 end groups are oxidized to carboxyls. Theoretically speaking, the chain can be ruptured at any point, and oxidation always produces the whole gamut of acids from formic acid to $\text{CH}_3(\text{CH}_2)_{36}-\text{COOH}$. In practice the conditions of oxidation are

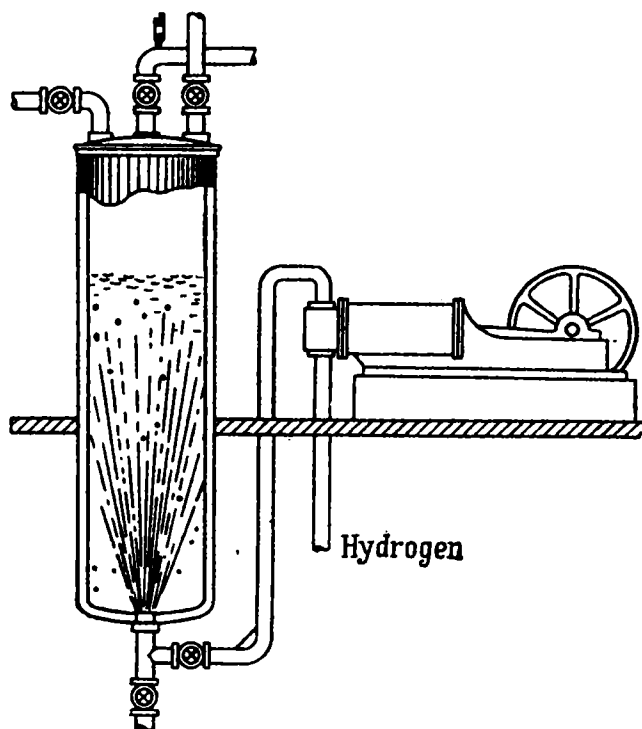
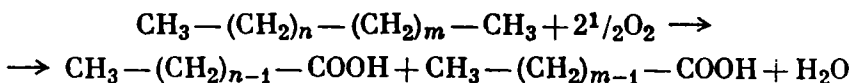


Fig. 48. Apparatus for hydrogenation of fats.

selected in such a way as to give the maximum yield of the acids suitable for soap-making (with 10 to 20 carbon atoms).

The principal reaction that takes place follows the equation:



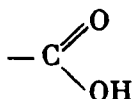
Oxidation is conducted in vertical columns filled with molten paraffin wax. Air is blown upwards through the melt, and small amounts of potassium permanganate are continually added to the upper part of the column. To avoid the formation of by-products, the process is interrupted when only 40% of the paraffin wax has been oxidized. The lower acids formed (formic, acetic, etc.) are washed away with water, and the reaction products are then treated with an alkali solution. The salts of the fatty acids are in this way transferred to the solution and separated from the unreacted paraffin wax. The

mixture of fatty acids is now acidified with sulphuric acid and divided into cuts by vacuum distillation.

Synthetic fatty acids are completely satisfactory substitutes in soap-making for acids produced from vegetable and animal fats. They differ from the natural acids only in the number of their carbon atoms. The natural acids always contain an even number of carbon atoms in the molecule, whereas the synthetic acids are mixtures of approximately equal amounts of acids with even and odd numbers of atoms in the molecule.

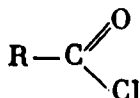
ACID CHLORIDES

126. Structure and Preparation of Acid Chlorides. By substituting a halogen for a hydroxyl group in alcohols we obtain alkyl halides (p. 135). The hydroxyl of the carboxyl group



like an alcohol hydroxyl, can be replaced by a halogen. This substitution gives rise to acid halides, of which the most important are the acid chlorides. *The chlorides of the carboxyl acids may thus be regarded as the products of the substitution of chlorine for the acid hydroxyls.*

The following are examples of acid chlorides: the chloride of acetic acid, or acetyl chloride, CH_3COCl , and the chloride of propionic acid, or propionyl chloride, $\text{C}_2\text{H}_5\text{COCl}$. The structure of the chlorides of the monoacids can be expressed by the general formula:



Acid chlorides are prepared by the action of phosphorus pentachloride or trichloride on carboxylic acids:

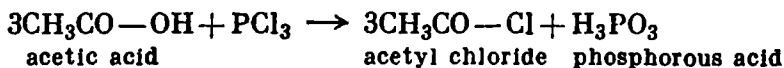


Fig. 49 shows an apparatus for the laboratory preparation of acetyl chloride. Fifty grams of anhydrous acetic acid are placed in a round-bottom flask with a side tube; 40 g of phosphorus trichloride are poured into a dropping funnel fixed in the stopper of the flask. The flask is placed in a water-bath and connected with the tube of a cooler; the other end of the tube is connected with a receiver. Phosphorus trichloride is allowed to drip into the water-cooled flask. The water-

bath is then heated, and the acetyl chloride formed is distilled off (b.p. 55°) into the receiver.

To prevent the acetyl chloride from interacting with the moisture of the air, a tube filled with calcium chloride is attached to the side-arm of the receiver.

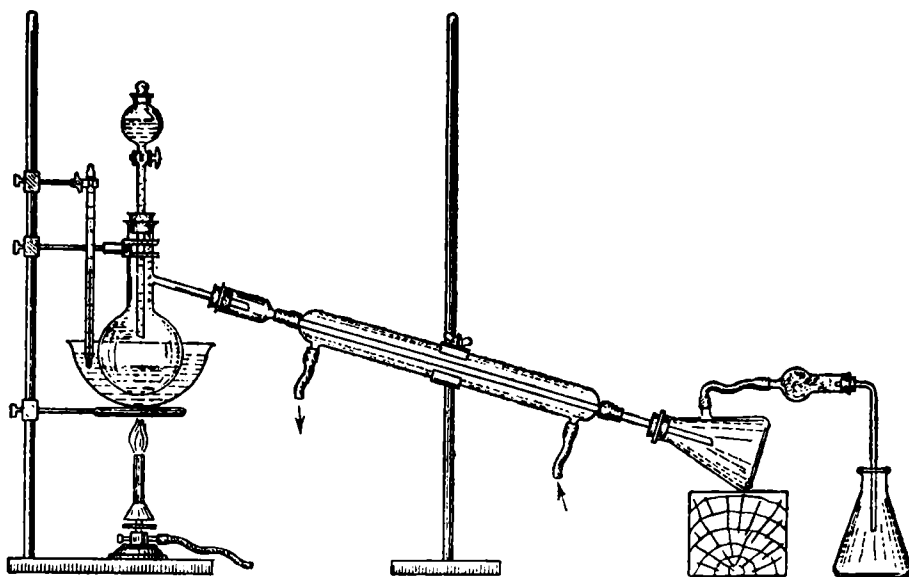
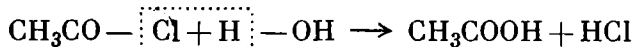


Fig. 49. Apparatus for laboratory preparation of acetyl chloride.

127. Properties of Acid Chlorides. The lower acid chlorides are liquids that are heavier than water; their vapours have a pungent odour and irritate the mucous membranes of the nose and the eyes.

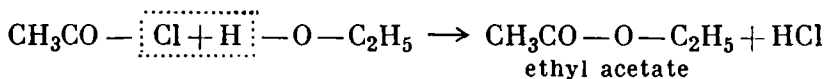
The most remarkable property of the acid chlorides is the exceptional mobility of their chlorine. For example, they are decomposed very quickly even by cold water, an acid and hydrogen chloride being formed:



The low-boiling acid chlorides fume in moist air. This is due to the fact that their vapours react with the moisture of the air according to the above equation, forming a mist of drops of hydrochloric acid and organic acids.

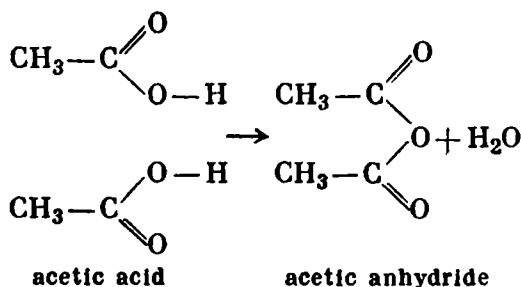
Acid chlorides of high molecular weight react with water less vigorously.

With alcohols, acid chlorides interact to produce esters:

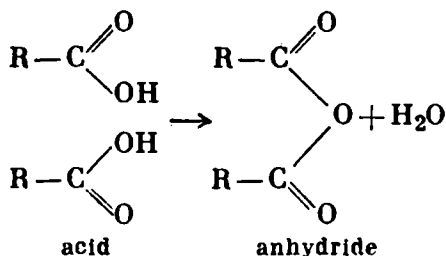


ACID ANHYDRIDES

128. Structure and Preparation of Acid Anhydrides. There are some substances that can be represented as the result of the removal of water from the hydroxyls of the carboxylic groups of two acid molecules. Such substances are called acid anhydrides:

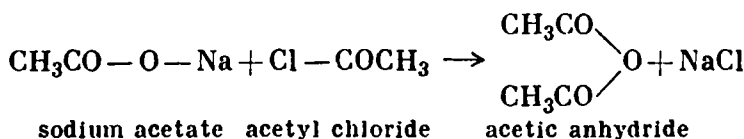


In general form this can be written as follows:



The reaction can be brought about by leading acid vapours over certain catalysts.

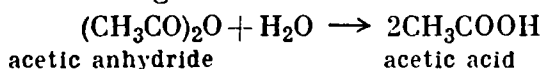
A method of preparing anhydrides that proves their structure consists in acting upon the sodium salt of an acid with an acid chloride, e.g.:



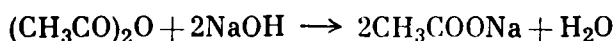
By means of this reaction Gerhardt in 1852 for the first time prepared monoacid anhydrides.

129. Properties of Acid Anhydrides. The lower acid anhydrides are liquids, which are insoluble in water and have a pungent odour.

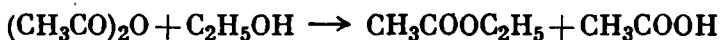
In chemical properties the anhydrides resemble the acid chlorides, but the reactions of the anhydrides, specifically with water, are less vigorous. For instance, the anhydrides are quickly decomposed by water only upon heating:



With alkalis the reaction proceeds more rapidly:



With alcohols anhydrides form esters:



Acetic anhydride is a liquid heavier than water; it boils at 140° . Large quantities of acetic anhydride are used to make artificial silk (acetate rayon).

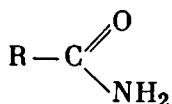
Formic anhydride is unknown; attempts to prepare it have failed because it immediately decomposes into CO and H_2O .

ACID AMIDES

130. Structure and Preparation of Acid Amides. *Acid amides are the products of the substitution of the ammonia radical (the amino-group NH_2) for the hydroxyl group of an acid.*

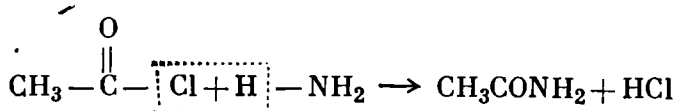
$\text{H} - \text{CO} - \text{NH}_2$	formic acid amide (formamide)
$\text{CH}_3 - \text{CO} - \text{NH}_2$	acetic acid amide (acetamide)
$\text{C}_2\text{H}_5 - \text{CO} - \text{NH}_2$	propionic acid amide (propionamide)
$\text{C}_3\text{H}_7 - \text{CO} - \text{NH}_2$	butyric acid amide (butyramide)

The general formula of the amides is:

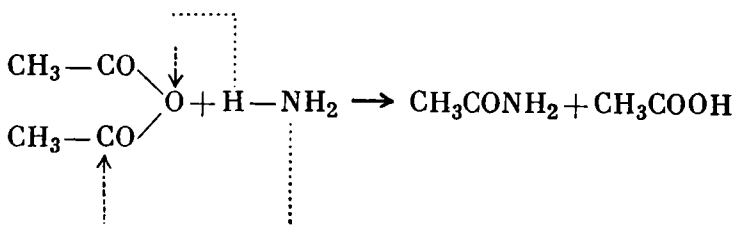


Amides can be prepared by the action of ammonia on other acid derivatives, e.g.:

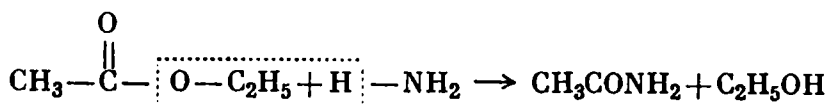
(a) *acid chlorides*



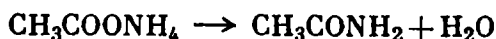
(b) *acid anhydrides*



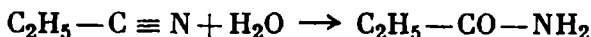
(c) esters



Amides can also be prepared by heating ammonium salts of carboxylic acids

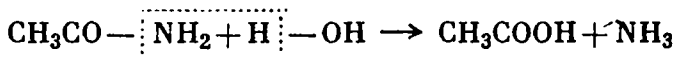


as well as by the partial hydrolysis of acid nitriles

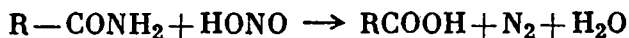


131. Properties of Acid Amides. The amides, with the exception of the liquid formamide, are crystalline. Unlike ammonia, they scarcely exhibit any basic properties. It is only with strong acids that they produce salts (for instance, $\text{CH}_3\text{CONH}_2 \cdot \text{HCl}$), which are easily decomposed by water. The amino-group hydrogen in amides can be replaced by a metal; in the case of acetamide, for example, we know the compound $(\text{CH}_3\text{CONH})_2\text{Hg}$.

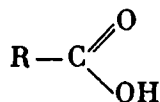
When boiled with water in the presence of acids or alkalis, the amides form ammonia and a corresponding acid:



The action of nitrous acid on amides releases nitrogen and produces a carboxylic acid:



132. Acid Derivatives and Radical. The structure of the acids is expressed by the formula:



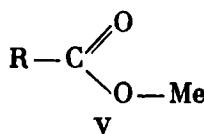
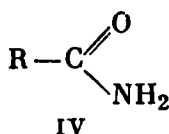
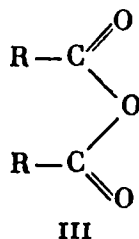
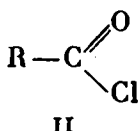
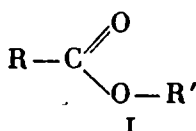
Esters may be regarded as the products of the substitution of a hydrocarbon radical for the hydroxyl hydrogen of an acid (formula I).

Acid chlorides are obtained by substituting chlorine for the hydroxyl; their structure is expressed by formula II.

Anhydrides are formed by the removal of water from the hydroxyls of two acid molecules and have a structure corresponding to formula III.

Amides are products of the substitution of the amino-group for the acid hydroxyl (formula IV).

Finally, it is clear that the structure of salts can be expressed by formula V (where Me is a metal).

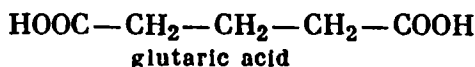
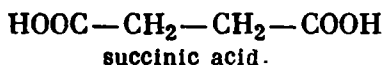
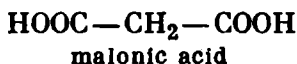
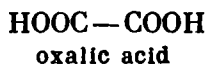


All these substances are thus derived from acids by changes in the hydroxyl group alone, while the R—CO— group of atoms remains unchanged. The substances derived from acids by changes in the hydroxyl group are called *acid derivatives*; the unchanged part of the molecule is called the *acid radical*, or *acyl*.

The formic acid radical H—CO— is called *formyl*; the acetic acid radical CH₃—CO— is called *acetyl*; the propionic acid radical C₂H₅—CO— is called *propionyl*; the butyric acid radical C₃H₇—CO— is called *butyryl*, etc.

SATURATED DICARBOXYLIC ACIDS

133. Structure of Saturated Dicarboxylic Acids. The following are examples of saturated dicarboxylic acids:

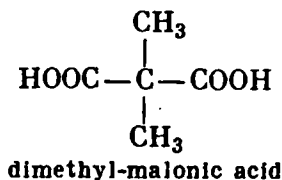
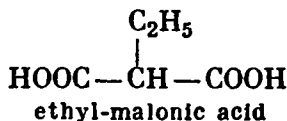
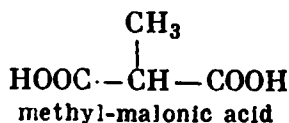
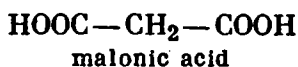


The saturated dicarboxylic acids, with the exception of oxalic acid, may be regarded as dicarboxylic derivatives of the saturated hydrocarbons C_nH_{2n+2}; their composition corresponds to the general formula C_nH_{2n}(COOH)₂.

The most important acids of this series are those in which the functional groups are at the end of a normal carbon chain, i.e., acids of the structure HOOC—(CH₂)_n—COOH.

By substituting alkyls for the methylene group hydrogen atoms in the molecules of these acids, we can obtain dicarboxylic acids with branched carbon atom chains. In this way malonic acid can

be made to yield a series of acids which are its direct homologues:



Similar series can be derived from succinic, glutaric, and other acids.

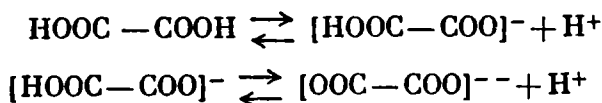
134. Physical and Chemical Properties of Saturated Dicarboxylic Acids. Table 11 lists the physical properties of some of the dicarboxylic acids.

TABLE 11. Physical Properties of Some Dicarboxylic Acids

Acid	Formula	M.p. for anhydrous substance, °C	Solubility in 100 g of water at 20° (in g)	First ionization constant
Oxalic	$\text{HOOC}-\text{COOH}$	189.5	8.6	3.8×10^{-2}
Malonic . . .	$\text{HOOC}-\text{CH}_2-\text{COOH}$	130.3	73.5	1.58×10^{-3}
Succinic . .	$\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$	182.8	5.8	6.65×10^{-5}
Glutaric . . .	$\text{HOOC}-(\text{CH}_2)_3-\text{COOH}$	97.5	63.9	4.75×10^{-5}
Adipic . . .	$\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$	153	1.5	3.71×10^{-5}
Pimelic . . .	$\text{HOOC}-(\text{CH}_2)_5-\text{COOH}$	105.5	5.0	3.49×10^{-5}
Suberic . . .	$\text{HOOC}-(\text{CH}_2)_6-\text{COOH}$	140	0.16	2.99×10^{-5}
Azelaic . . .	$\text{HOOC}-(\text{CH}_2)_7-\text{COOH}$	107.5	0.24	2.53×10^{-5}
Sebacic . . .	$\text{HOOC}-(\text{CH}_2)_8-\text{COOH}$	134.5	0.10	2.38×10^{-5}

The saturated dicarboxylic acids are crystalline substances. Like the monoacids (p. 210), the saturated diacids with an even number of carbon atoms melt at higher temperatures than the neighbouring homologues with odd numbers of carbon atoms. The odd acids have a much higher solubility in water than the even, with solubility diminishing as the number of carbon atoms increases.

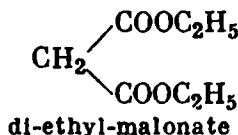
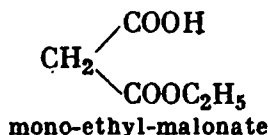
The diacids undergo consecutive dissociation:



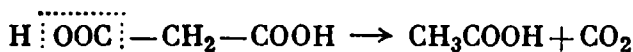
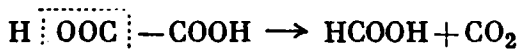
The diacids are stronger than the corresponding monoacids. The dissociation of oxalic acid into ions is especially pronounced. The

degree of ionization of the diacids drops with the rise of their molecular weight.

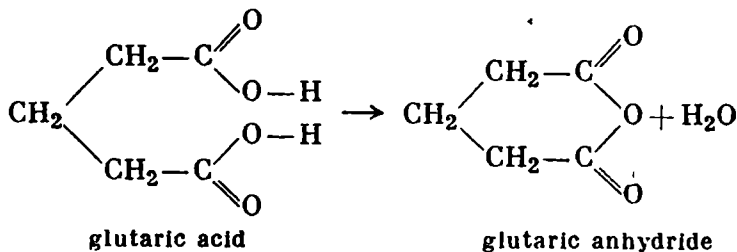
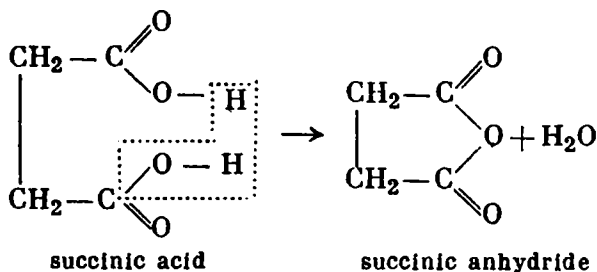
Since the diacid molecule contains two carboxyls, the acids give rise to two series of derivatives: normal and acid salts and esters:



When oxalic or malonic acid is heated, CO_2 is evolved:



The diacids with four or five carbon atoms, i.e., succinic and glutaric acids, upon heating give up the elements of water and form inner cyclic anhydrides:



In the molecules of these anhydrides the chain of four or five carbon atoms forms a ring through the oxygen atom.

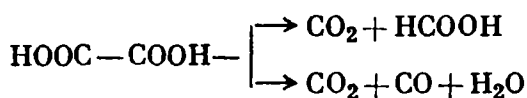
The ability of succinic and glutaric acids to form cyclic anhydrides is easily explained in terms of van't Hoff's tetrahedral model. In the chelate configuration of carbon atoms (Fig. 24a and b on p. 153), the terminal links of the chain of four—and, especially, of five—atoms are very close to each other. If there are hydroxyl groups at the ends of the chain (as in the case of succinic and glutaric acids), the oxygen, whose valency bonds are at some angle (p. 65), easily closes the ring. The stability of cycles is considered in greater detail in the section on alicyclic compounds (p. 508).

135. Oxalic Acid. Oxalic acid (ethanedioic acid) $\text{HOOC}-\text{COOH}$ is the simplest of the dicarboxylic acids. It is highly widespread in nature: potassium hydrogen oxalate $\text{HOOC}-\text{COOK}$ occurs in sorrel and oxalis, and calcium oxalate $(\text{COO})_2\text{Ca}$ has been found in many plants.

The first representative of a homologous series, oxalic acid, like formic acid, differs both in structure and chemical character from the other acids. Indeed, all the carboxylic acids—acetic, propionic, stearic, etc.—can be regarded as derivatives of hydrocarbons, with a hydrogen replaced by a carboxyl. Formic acid and oxalic acid, however, do not fit into this definition. Formic acid is a combination of a carboxyl and a hydrogen atom, while oxalic acid can be looked upon as a combination of two linked carboxyls. The properties of the two acids display much similarity.

Oxalic acid crystallizes with two molecules of water: $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. It can also be obtained in the form of anhydrous hygroscopic crystals.

When heated rapidly, the acid decomposes:



When it is heated in the presence of sulphuric acid, the only reaction products are carbon dioxide, carbon monoxide, and water.

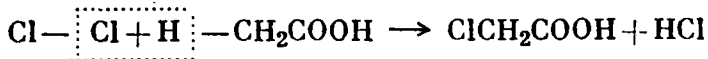
It is characteristic of oxalic acid that it oxidizes readily. On oxidation, it yields carbon dioxide and water.

The acid is a product of the oxidation of many organic substances. One of the methods of its commercial preparation is by the treatment of sawdust by alkalis, with the simultaneous oxidation of the products by the oxygen of the air.

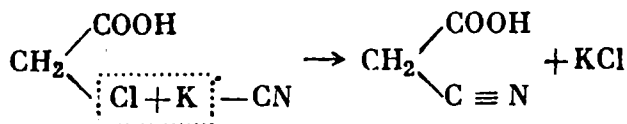
Oxalic acid is a rather strong acid: its ionization constant is about 2,000 times greater than that of acetic acid.

The acid and its salts (oxalates) are used in calico printing, as well as to remove dust stains from fabrics.

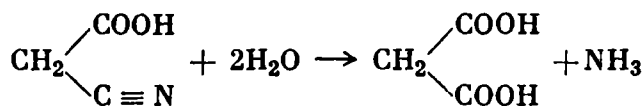
136. Malonic Acid. Malonic acid $\text{HOOC}-\text{CH}_2-\text{COOH}$ has been found in turnip juice. For its synthetic preparation one of the hydrogen atoms in acetic acid is replaced by chlorine to yield chloroacetic acid:



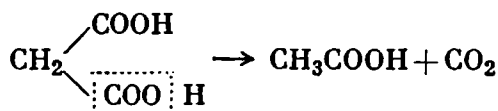
The interaction of the chloroacetic acid with potassium cyanide then produces cyanoacetic acid:



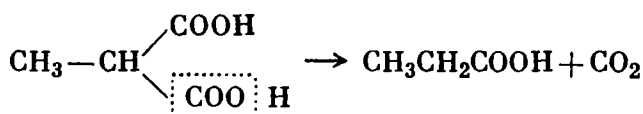
Subsequent saponification yields malonic acid:



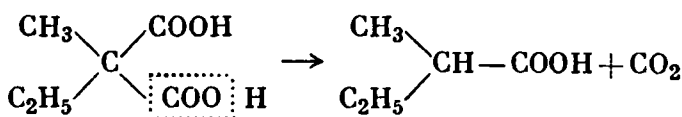
When malonic acid is heated somewhat above its melting point, it loses carbon dioxide and turns into acetic acid:



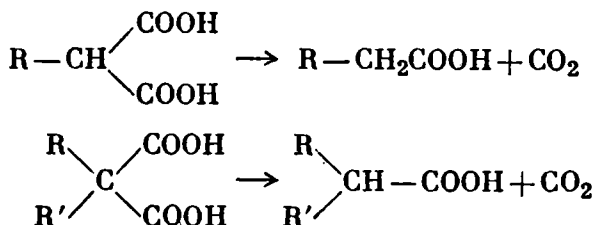
The alkylmalonic acids, when heated above their melting points, similarly lose CO_2 , turning into alkylacetic acids. For example, methylmalonic acid yields methylacetic, i.e., propionic acid:



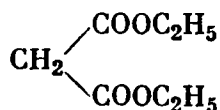
Methylethylmalonic acid is converted into methylethylacetic acid, i.e., an isomer of valeric acid:



In general form this transformation can be expressed by the equations:

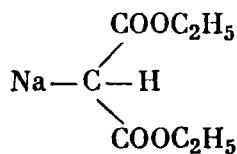


137. Syntheses Involving Malonic Ester. The most important of the malonic acid derivatives is ethyl malonate, usually called simply malonic ester:



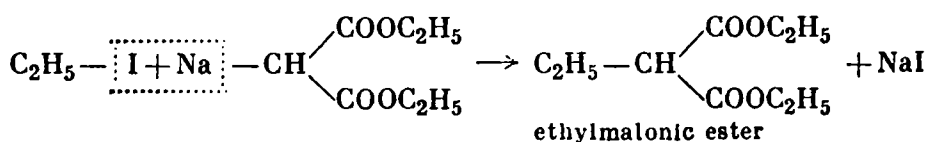
This is a liquid with a fruity odour, which boils at 199° . Malonic ester is used extensively in the laboratory for various syntheses.

The remarkable thing about this compound is the fact that the methylene group hydrogen can be replaced by sodium, with the formation of sodiomalonic ester:

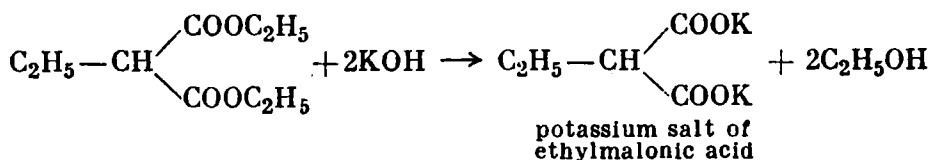


Sodiummalonic ester is prepared by means of sodium ethoxide.

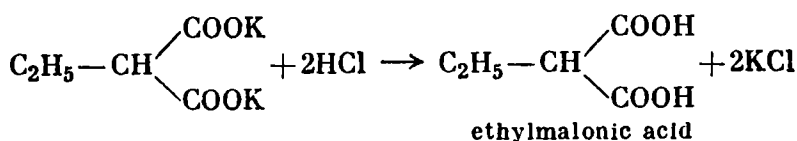
The action of alkyl halides upon sodiummalonic ester produces esters of substituted malonic acids, e.g.:



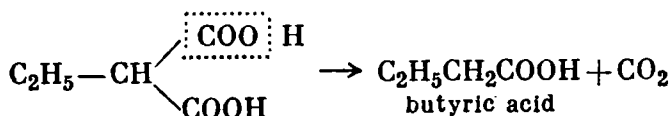
The saponification of this ester by potassium hydroxide yields the potassium salt of ethylmalonic acid:



The free acid is easily prepared from the salt:

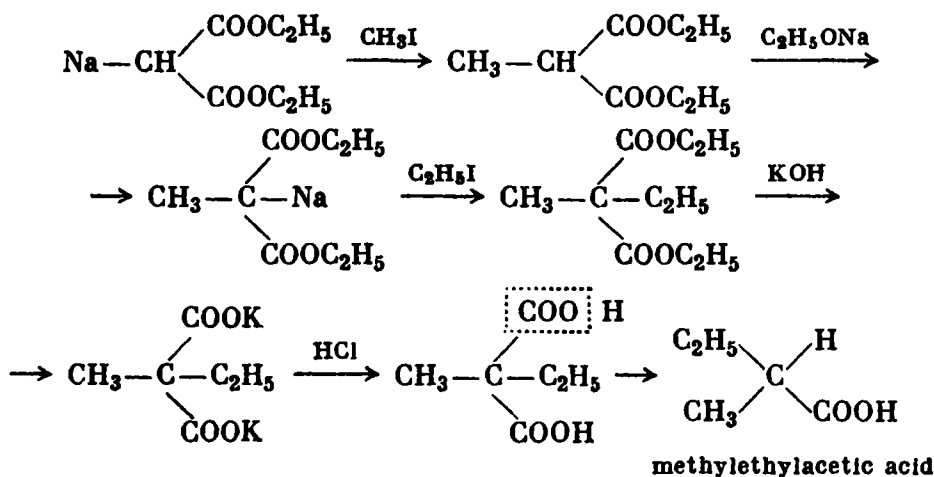


When ethylmalonic acid is heated, it loses a molecule of CO_2 forming butyric acid:

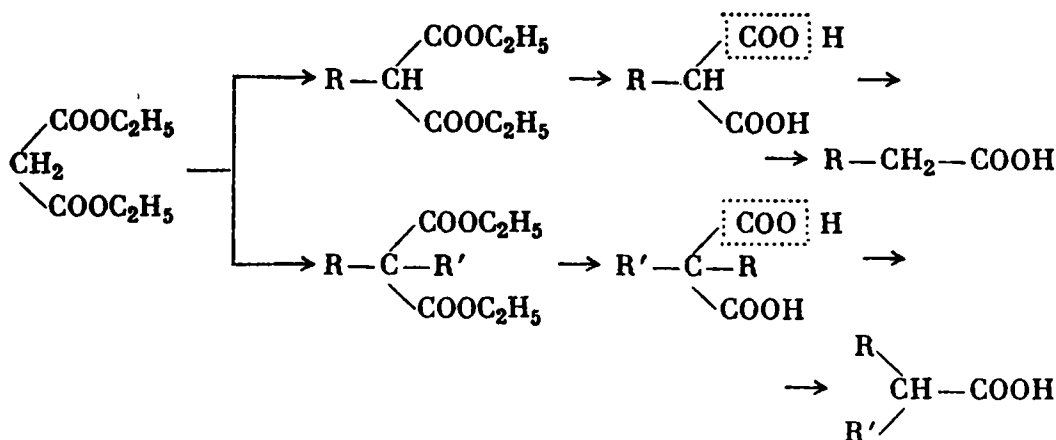


The second hydrogen atom in the mono-substituted malonic ester molecule can likewise be replaced by a sodium atom, and a hydrocarbon radical can also be substituted for the latter.

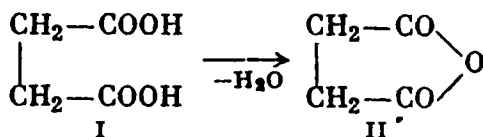
The synthesis of one of the isomers of valeric acid, methylethylacetic acid, serves as an example of this:



In general form the preparation of substituted acetic acid by means of malonic ester may therefore be expressed by the following equation:



138. Succinic Acid. Succinic acid (I) was originally prepared by the distillation of amber; it occurs in brown coal and in many plants. Its distillation produces succinic anhydride (II):

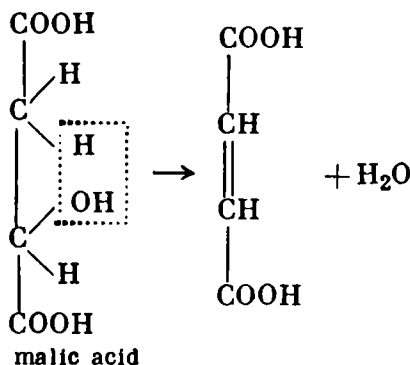


Succinic anhydride is a crystalline substance (m.p. 120°; b.p. 261°). It is soluble in water; in the cold, however, it merely adds water slowly, forming succinic acid.

UNSATURATED DICARBOXYLIC ACIDS

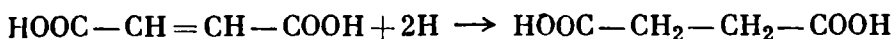
139. Fumaric and Maleic Acids. Fumaric acid $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$, the simplest of the unsaturated dicarboxylic acids, occurs in the weed *Fumaria officinalis* and in many moulds. Maleic acid, whose composition is expressed by the same formula, may be prepared synthetically.

Both acids may be obtained by heating malic acid:



The product, when malic acid is heated slowly, is mainly fumaric acid, while maleic acid* predominates if heating is more intense.

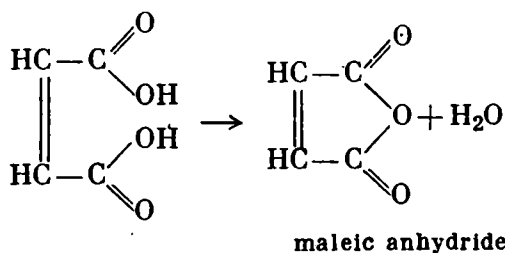
That both acids have the same structure is confirmed by their reduction to succinic acid:



But despite their identical structure, the two acids have markedly different properties.

Fumaric acid is a crystalline substance, which, without melting, sublimes at 200° and dissolves in water poorly. Maleic acid melts at 130° , dissolves in water very readily, and is the stronger acid. It has not been found in nature.

When heated, maleic acid readily loses water, forming maleic anhydride:



The anhydride is a needle-like crystal substance (m.p. 52.6° ; b.p. 202°). When treated with water, it slowly forms maleic acid.

* Maleic acid derives its name from malic acid.

When fumaric acid is heated to 300° , it too loses water and forms maleic anhydride. No fumaric anhydride, i.e., a substance that would produce fumaric acid when treated with water, is known.

Maleic acid is unstable; in the presence of catalysts (such as traces of iodine or traces of nitrous acid) it is converted into fumaric acid. The heat of combustion of maleic acid is greater than that of fumaric acid; hence, energy is generated when maleic acid is converted into fumaric. The maleic acid esters are readily converted into fumaric acid esters in the presence of a small amount of iodine.

Maleic dimethylate in the presence of a small quantity of diethylamine $(C_2H_5)_2NH$ is converted into a fumaric acid ester at almost

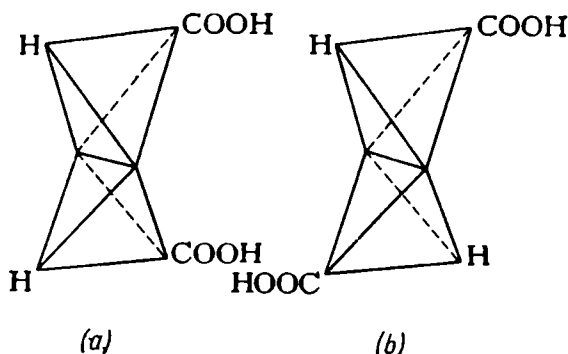
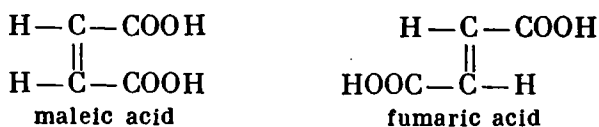


Fig. 50. Fumaric and maleic acid stereoisomerism:
a—maleic acid; b—fumaric acid.

the speed of an ionic reaction; this is accompanied by the generation of a considerable amount of heat. All this indicates that fumaric acid is the poorer of the two acids in energy.

The conversion of fumaric acid into maleic involves the absorption of energy. It takes place when fumaric acid is exposed to ultra-violet irradiation. The relationship between fumaric acid (Fig. 50b) and maleic (Fig. 50a) is the same as between crotonic acid and isocrotonic acid or between oleic acid and elaidic acid; they are *cis*- and *trans*-isomers:



The choice of formula for each of the acids is based on the fact that when maleic acid loses water it forms an inner anhydride, whereas fumaric acid is not known to have an anhydride. It is obvious that a cyclic anhydride can be formed only if both carboxyls are in *cis*-position. Consequently, maleic acid is the *cis*-isomer, while fumaric acid is the *trans*-isomer. The correctness of this conclusion is borne out by other properties of these acids.

Halogenated Acids

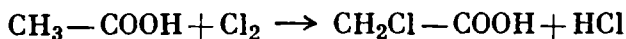
140. Structure and Preparation of Halogenated Acids. Halogenated acids are prepared by substituting a halogen for one or several hydrogen atoms linked to carbon in carboxylic acids. The following are examples of halogenated acids:

$\text{CH}_2\text{Cl}-\text{COOH}$	monochloroacetic acid
$\text{CHCl}_2-\text{COOH}$	dichloroacetic acid
CCl_3-COOH	trichloroacetic acid

The initial letters of the Greek alphabet are used to indicate the position of the halogen substituents. The carbon atom linked to the carboxyl is designated by the Greek letter α (alpha), and subsequent atoms, by the letters β (beta), γ (gamma), δ (delta), etc. This is illustrated by the following examples:

$\overset{\beta}{\text{CH}_3}-\overset{\alpha}{\text{CH}_2}-\text{COOH}$ propionic acid	$\text{CH}_3-\text{CHCl}-\text{COOH}$ α -chloropropionic acid
	$\text{CH}_2\text{Cl}-\text{CH}_2-\text{COOH}$ β -chloropropionic acid
$\overset{\gamma}{\text{CH}_3}-\overset{\beta}{\text{CH}_2}-\overset{\alpha}{\text{CH}_2}-\text{COOH}$ butyric acid	$\text{CH}_3-\text{CH}_2-\text{CHCl}-\text{COOH}$ α -chlorobutyric acid
	$\text{CH}_3-\text{CHCl}-\text{CH}_2-\text{COOH}$ β -chlorobutyric acid
	$\text{CH}_2\text{Cl}-\text{CH}_2-\text{CH}_2-\text{COOH}$ γ -chlorobutyric acid

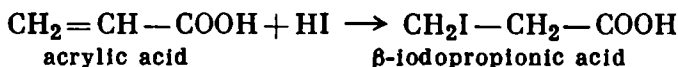
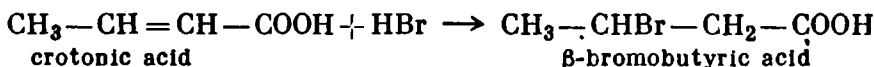
The α -halogenated acids can be prepared by the direct action of a halogen on acids:



The chlorination and bromination of the saturated monoacids was studied by Markovnikov in 1868-70. He demonstrated that halogenation proceeds in the presence of halogen carriers (iodine) and results in the substitution of α -hydrogens.

Another method of preparing halogenated acids that deserves mention is the addition of hydrogen halides to unsaturated acids. In this case, if the multiple bond links a carbon atom next to the

carboxyl, the halogen is added to the carbon atom in β -position to the carboxyl:



In the latter case addition does not obey Markovnikov's rule.

141. Properties of Halogenated Acids. Halogenated acids enter into all the reactions characteristic of carboxylic acids. The introduction of a halogen into the acid molecule makes acidic properties more pronounced: monochloroacetic acid is stronger than acetic acid, dichloroacetic acid is stronger than monochloroacetic acid, and trichloroacetic acid is a very strong acid.

The increased acidity is due to the fact that the halogen atom draws towards itself the electrons not only of neighbouring, but also of more remote atoms. The proton is therefore more easily detached from the molecule, i.e., ionization is facilitated. The halogen in α -position has the strongest effect; with increased distance from the carboxyl, the influence of the halogen weakens.

	Ionization constant
α -chlorobutyric acid	140×10^{-5}
β -chlorobutyric acid	8.9×10^{-5}
γ -chlorobutyric acid	2.6×10^{-5}
butyric acid	1.55×10^{-5}

Monochloroacetic acid is the most important industrially. It is prepared by chlorinating acetic acid; enormous quantities of it are used in the synthesis of indigo and many other substances. Monochloroacetic acid is a colourless crystalline substance, which deliquesces in the air (m.p. 61.5° ; b.p. 189°).

Monochloroacetic acid, as well as trichloroacetic acid, was first prepared by Lovits in 1793.

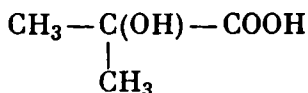
Hydroxy Acids

The hydroxy acids are substances containing both an alcoholic hydroxyl and a carboxyl group in the molecule.

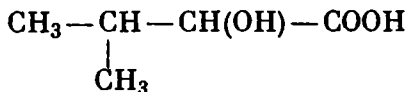
The following are examples of hydroxy acids:

Hydroxyacetic, or glycolic, acid	$\text{CH}_2(\text{OH})-\text{COOH}$
α -Hydroxypropionic, or lactic, acid	$\text{CH}_3-\text{CH}(\text{OH})-\text{COOH}$
β -Hydroxypropionic acid	$\text{CH}_2(\text{OH})-\text{CH}_2-\text{COOH}$
γ -Hydroxybutyric acid	$\text{CH}_2(\text{OH})-\text{CH}_2-\text{CH}_2-\text{COOH}$

In the Geneva nomenclature the names of the hydroxy acids are formed by introducing the suffix *ol* to denote the presence of the hydroxy group in the corresponding part of the molecule. Glycolic acid, for example, becomes ethanol-oic acid, while the α - and β -hydroxypropionic acids become propanol-2-oic and propanol-3-oic acids respectively. Structural formulas are easily derived from the names. For instance, 2-methylpropanol-2-oic acid has the structural formula



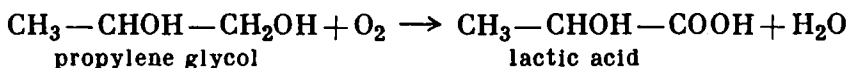
while 2-methylbutanol-3-oic acid has the structural formula



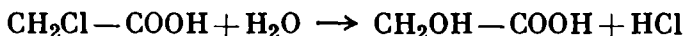
Hydroxy acids are characterized by the number of carboxyl groups (basicity) and the number of hydroxyl groups (not including the hydroxyls of the carboxyl groups). The above acids are thus monocarboxylic monohydroxy acids, whereas malic acid $\text{HOOC}-\text{CH}_2-\text{CH}(\text{OH})-\text{COOH}$ is a dicarboxylic monohydroxy acid.

142. Preparation of Hydroxy Acids and Their Structure. The joint presence of hydroxyl and carboxyl groups in the hydroxy acids makes it possible to obtain these compounds both from alcohols and from acids.

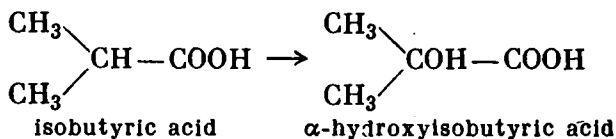
1. Oxidation of glycols:



2. Replacement of a halogen in halogenated acids by a hydroxyl. This takes place when halogenated acids are boiled with water or with an alkali:



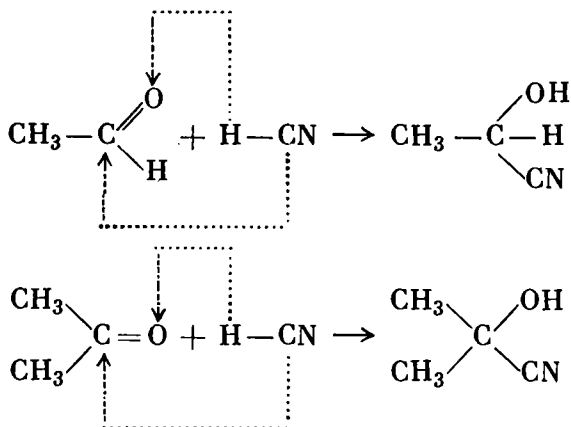
3. Oxidation of acids with a tertiary carbon atom in α -position to the carboxyl by potassium permanganate:



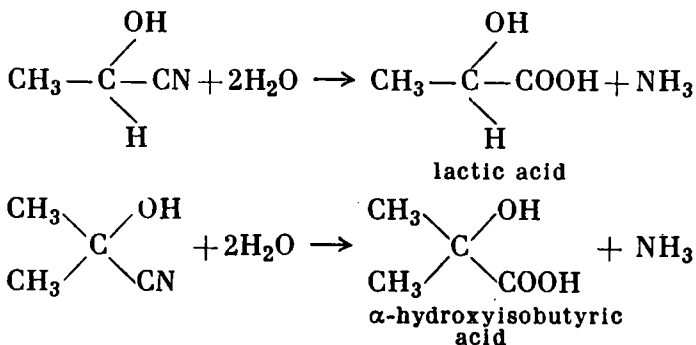
4. Oxidation of fatty acids in β -position (see p. 214).

5. A highly important method of preparing hydroxy acids is their preparation from aldehydes and ketones.

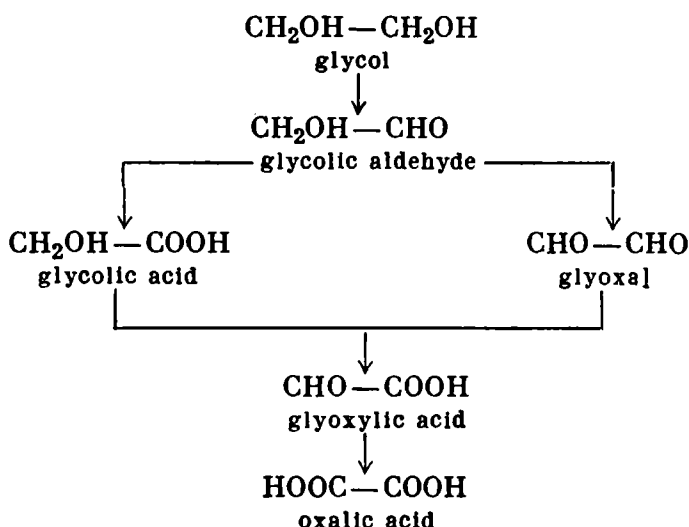
Aldehydes and ketones are capable of adding hydrogen cyanide:



The reactions produce hydroxynitriles (cyanohydrins), whose saponification yields α -hydroxy acids:

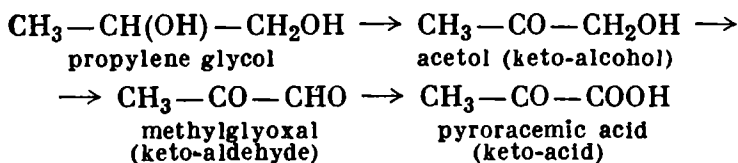


143. Oxidation of Polyhydroxy Alcohols. When ethylene glycol $\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$ is oxidized, each of the CH_2OH groups characteristic of a primary alcohol may be oxidized either to a CHO aldehyde group or to a COOH carboxyl. This gives rise to substances whose formulas and names are given on the following scheme:

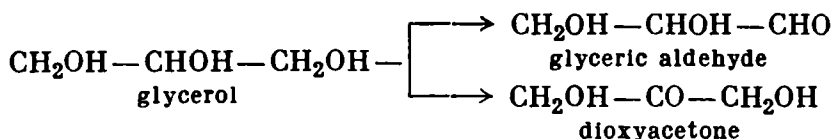


Glycolic aldehyde is both an aldehyde and an alcohol; glycolic acid is an alcohol and an acid, and glyoxylic acid is an aldehyde and an acid.

Propylene glycol $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2\text{OH}$ contains CH_2OH and $\text{CH}(\text{OH})$ groups; the latter group is, of course, characteristic of secondary alcohols, which upon oxidation yield ketones. Therefore the oxidation of propylene glycol can yield a series of substances which, although alcohol, aldehyde, or acid, are at the same time ketones:



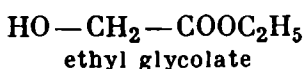
The initial products of the oxidation of glycerol are glyceric aldehyde and dioxyacetone:



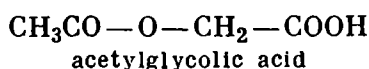
In this way the oxidation of polyhydroxy alcohols can produce series of substances with mixed functions: aldehyde alcohols, keto-alcohols, keto-aldehydes, alcohol acids (hydroxy acids), aldehyde acids, etc.

144. Properties of Hydroxy Acids. The hydroxy acids are crystalline substances, which dissolve easily in water. They melt at higher temperatures and dissolve in water more readily than corresponding fatty acids. The hydroxy acids also have higher ionization constants.

The presence of both a carboxyl and a hydroxyl group in the molecule has the effect that these compounds can react either as alcohols or as acids. With ethyl alcohol, for instance, glycolic acid forms an ester, ethyl glycolate:

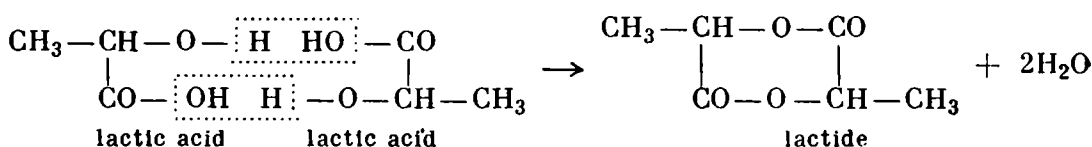


At the same time there is an ester formed by glycolic acid (as an alcohol) with acetic acid:



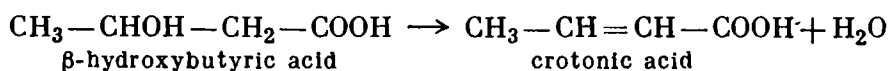
The hydroxy acids more or less readily lose water to form diverse substances, depending on the position of the hydroxyl.

1. Alpha-hydroxy acids, upon being heated, lose water readily, forming cyclic esters, whose six-membered ring consists of four carbon atoms and two oxygen atoms. Mutual esterification in this case takes place between the hydroxyl and carboxyl groups of two acid molecules. The resulting esters have been named *lactides* (from lactic acid):

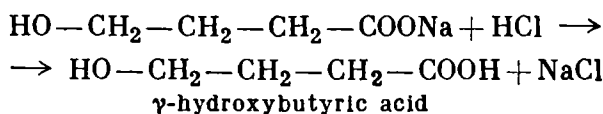


Lactides are crystalline substances. When boiled with water, they are saponified with the formation of the initial hydroxy acid.

2. Beta-hydroxy acids, upon being heated, lose water to form unsaturated acids:

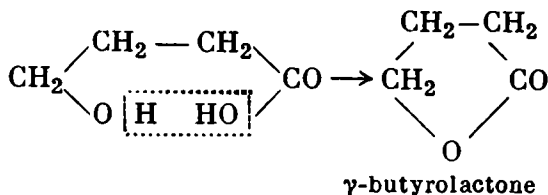


3. Gamma- and δ -hydroxy acids are very unstable in the free state, and most of them are known only as salts. The action of other acids upon these salts should produce the hydroxy acids themselves, e.g.:



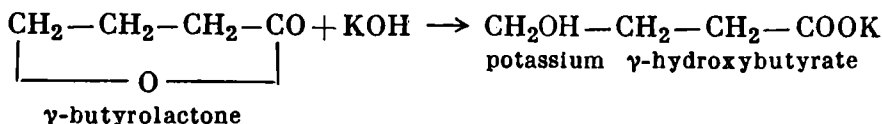
But the moment the hydroxy acids are formed, they are converted, owing to the spatial proximity of the hydroxyl and carboxyl OH

groups, into five- and six-membered cyclic *lactones*:



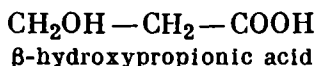
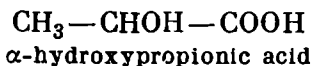
The lactones are cyclic esters. They are usually liquids or low-melting solids, which may be distilled without decomposing.

An alkali ruptures the lactone ring to form a salt:

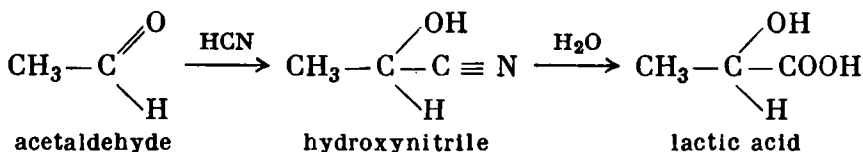


Butyrolactone was first prepared by A. Zaitsev in 1873.

145. Lactic Acid. Lactic, or hydroxypropionic, acid $\text{CH}_3 - \text{CH}(\text{OH}) - \text{COOH}$ was discovered in 1780 by Scheele in sour milk. Two isomers of hydroxypropionic acid are possible:

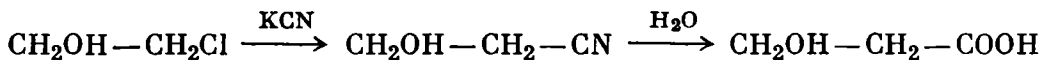


The synthesis of lactic acid from acetaldehyde and hydrogen cyanide made it possible to establish its structure:



In acetaldehyde the oxygen is linked with only one carbon atom; consequently, in lactic acid the hydroxyl and the carboxyl must be attached to the same carbon atom. Lactic acid is therefore the α -hydroxypropionic acid.

Its isomer, β -hydroxypropionic acid, was first prepared by Wurtz from ethylene chlorohydrin:

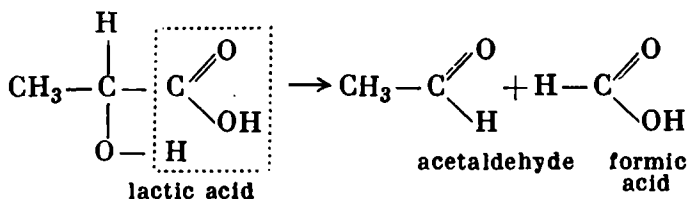


As may be seen from the structural formula of lactic acid $\text{CH}_3 - \text{CH}(\text{OH}) - \text{COOH}$, its molecule contains an asymmetric carbon atom. Optically active forms are therefore known for this acid.

Dextrolactic acid and laevolactic acid melt at $25\text{--}26^\circ$ and are optical antipodes, i.e., they rotate the plane of polarization of light in opposite directions. Besides this, inactive lactic acid is also known, a thick syrup, which, when evaporated at a greatly reduced

pressure, solidifies to crystals that melt at 18° . The inactive, racemic acid can be obtained by mixing equal quantities of D- and L-lactic acids* and is evidently a compound of them.

When heated with dilute sulphuric acid, lactic acid decomposes, yielding acetaldehyde and formic acid:



If the heating is done in the presence of concentrated sulphuric acid, the resulting formic acid is further broken down with the evolution of carbon monoxide.

Decomposition with the formation of formic acid is a characteristic property of the α -hydroxy acids.

Lactic acid is used in the leather industry, in the dyeing of textiles, and in other industries.

Inactive lactic acid is formed in the lactic fermentation of saccharoid substances, in the curdling of milk, the preparation of sauerkraut, and the ensilage of vegetable feeding stuffs. Lactic acid is also formed when glucose is heated with a sodium hydroxide solution.

Laevolactic acid is formed in fermentation caused by certain bacteria.

Dextrolactic acid occurs in muscles and plays an important part as a product of metabolism in them. It was discovered by J. Liebig** in 1837 and is known as sarcolactic acid.

Wislicenus in 1869 pointed out that the explanation of the isomerism of lactic and sarcolactic acids, possessing identical structures, should be sought in the spatial configuration of the atoms inside their molecules. Wislicenus's paper (published in 1873) suggested to van't Hoff, according to his own words, the ideas that found embodiment in his stereochemical theory.

* These designations are explained in detail in Sec. 152 and Sec. 159.

** Justus von Liebig (1803-73) was an outstanding German chemist. He was a professor of the University of Giessen, where he founded a large chemical school.

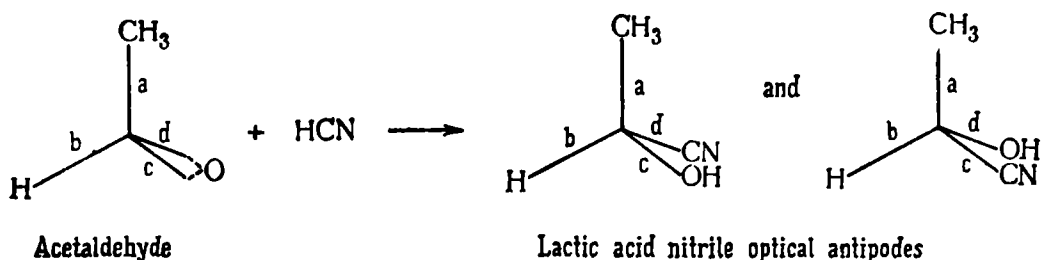
Liebig developed the methods and apparatus for estimating carbon and hydrogen by burning the substance in a refractory tube with copper oxide (1831). He also determined the composition of very many organic substances. Furthermore, mention should be made of his investigations of the fulminic acid derivatives and his joint paper with Wöhler on benzaldehyde ("oil of bitter almonds") and the derivatives of the benzoyl radical (1832). Liebig also studied the action of chlorine on alcohol; he prepared and studied acetaldehyde, chloral, and chloroform.

In recent years accurate physical methods have made it possible to establish the exact spatial configuration of the hydroxy acids. It has been found that D-lactic acid, according to our system of nomenclature (p. 151), is 2 σ -hydroxypropionic acid, while the L-acid is 2 ρ -hydroxypropionic acid.

Chemical syntheses produce the inactive lactic acid, i.e., a mixture of equal quantities of the D- and L-antipodes. This is also the case when other substances with an asymmetric carbon atom are prepared in the laboratory from optically inactive compounds. The reason for this is that the probability of the formation of each of the antipodes is absolutely the same.

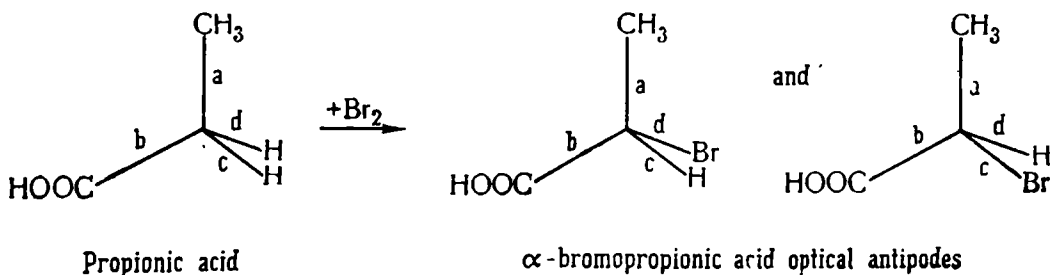
Let us consider three cases of the formation of molecules with an asymmetric carbon atom.

1. *Addition Reaction.* The addition of hydrogen cyanide to acetaldehyde results in lactic acid nitrile:



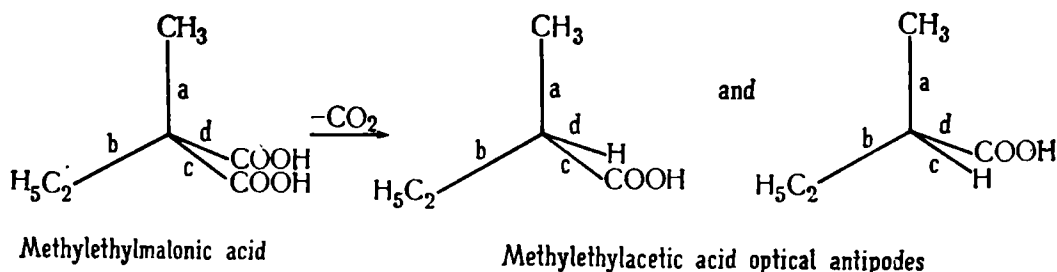
This is accompanied by the rupture of one of the bonds linking the oxygen atom to the carbon atom: either bond d (in which case the oxygen atom remains linked to the carbon atom by bond c) or bond c (in which case bond d remains). In either case we get a molecule with an asymmetric carbon atom, but the two molecules are like an asymmetric object and its mirror image and are therefore molecules of optical antipodes. The c and d bonds are perfectly identical, and there is absolutely the same probability of the rupture of one or the other. Hence, the two antipodes are formed in equal quantities and the resulting lactic acid is optically inactive.

2. *Substitution Reaction.* Alpha-bromopropionic acid can be prepared by brominating propionic acid:



The bromine atom can replace the hydrogen atom either at the d bond or at the c bond. The two bonds are identical, and the probability of the formation of each of the antipodes is absolutely the same.

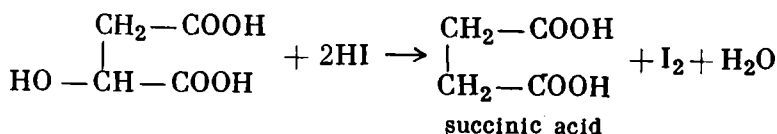
3. *Decomposition Reaction.* When methylethylmalonic acid loses CO_2 , methylethylacetic acid is formed. One of the carbon atoms in this case becomes asymmetric:



Since the probability of the CO_2 breaking away at the d bond and the c bond is absolutely the same, the antipodes are formed in equal quantities.

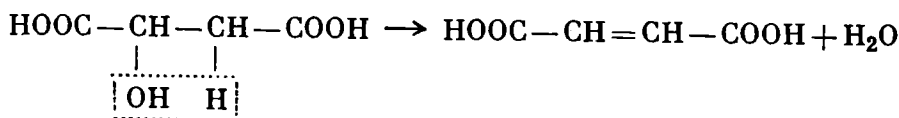
146. Malic Acid. Malic acid, as evident from its formula $\text{HOOC}-\text{CH}_2-\text{CH}(\text{OH})-\text{COOH}$, may be regarded as a derivative of succinic acid $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{COOH}$ in whose molecule one hydrogen atom has been replaced by a hydroxyl; it is hydroxysuccinic acid.

This is confirmed by the formation of succinic acid by the reduction of malic acid:

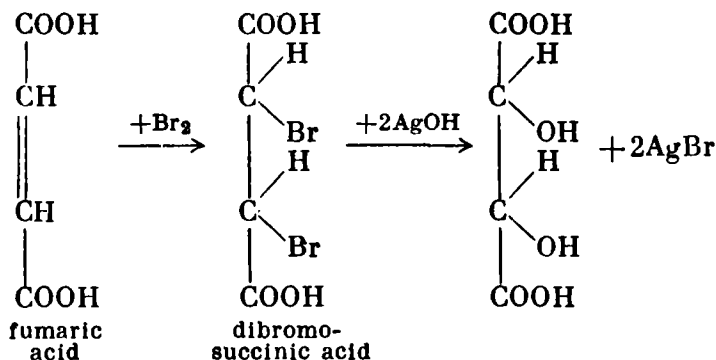


Both dextromalic acid and laevomalic acid melt at 100° ; they differ only in optical properties. Inactive malic acid melts at $130-131^\circ$; it is a compound of the molecules of the D- and L-acids. Laevomalic acid is found in unripe mountain-ash berries, apples, grape juice, etc.

When heated above its melting point, malic acid loses a molecule of water, turning into fumaric and maleic acids:

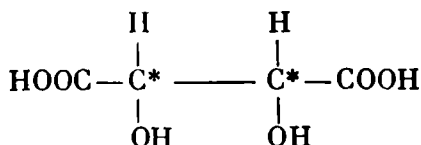


147. Tartaric Acids. Tartaric acid $C_4H_6O_6$ can be obtained from fumaric acid in the following way:



Consequently, it is a derivative of succinic acid, in whose molecule two hydrogen atoms have been replaced by two hydroxyls; it is dihydroxy succinic acid.

The tartaric acid molecule contains two identical asymmetric carbon atoms:



This permits of several stereoisomers:

1. Dextrorotatory (+ tartaric), or D-tartaric, acid. The dextrorotatory effect is due to the total dextrorotation of both asymmetric atoms.

2. Laevorotatory (— tartaric), or L-tartaric, acid. The laevorotatory effect is due to the total laevorotation of both asymmetric atoms.

3. Racemic acid. It is optically inactive, consisting of equal quantities of the D- and L-acids.

4. Mesotartaric acid. It too is optically inactive, this being due to the fact that one asymmetric centre in its molecule corresponds in configuration (and in rotation) to the D-acid, while the other corresponds to the L-acid. In this way the dextrorotation of one half of the molecule is compensated by the laevorotation of the other half. Mesotartaric acid cannot therefore be resolved into optically active forms.

The spatial distribution of the atoms in the tartaric acid molecules is represented in Fig. 51.

To make certain that the configuration of the groups linked with both carbon atoms in the optically active tartaric acid molecule is identical, one has but to slice the drawing by a horizontal plane running through the vortices of the tetrahedra and then turn the

upper tetrahedron vortex up, placing it on its base beside the bottom tetrahedron.

By projecting the models of the spatial distribution of the atoms in the tartaric acid molecules on a plane, we obtain the following

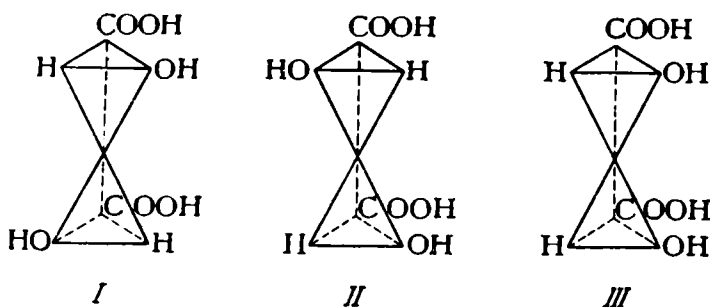
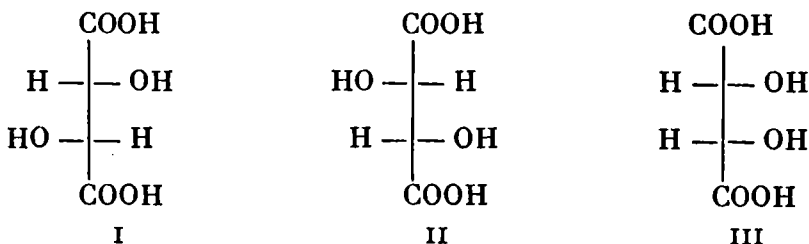


Fig. 51. Spatial distribution of atoms in tartaric acid molecules:
I—*D*-tartaric (dextrorotatory) acid; *II*—*L*-tartaric (laevorotatory) acid; *III*—mesotartaric acid.

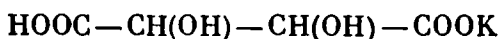
formulas, in which the points of intersection of the lines designate asymmetric carbon atoms:



Dextrorotatory and laevorotatory tartaric acids, i.e., *D*-tartaric and *L*-tartaric acids, are optical antipodes: the former in solution rotates the plane of polarization of a beam of light to the right, the latter, through an equal angle to the left. In addition to this, they form crystals that are mirror images of one another and cannot be superimposed. Both acids melt at 170° .

Dextrorotatory tartaric acid occurs very extensively in nature; it is contained in especially large quantities in grape juice. When grape juice undergoes fermentation, the acid forms a deposit called argol, which consists of potassium acid tartrate with a small amount of calcium tartrate. To obtain tartaric acid, argol is treated with acids; the acid thus isolated is purified by recrystallization. The dextro acid crystallizes in big transparent prisms. It dissolves readily in water and alcohol. Tartaric acid salts are called *tartrates*.

Potassium acid tartrate



is used as a mordant in fabric dyeing and printing. The salt has a low solubility in water and an even lower solubility in alcohol.

Tartar emetic



is used as a mordant in dyeing and calico printing, as well as in medicine.

Rochelle salts



are used in medicine and in laboratory work.

When a copper salt solution (say, a solution of blue vitriol) is added to an alkaline solution of tartaric acid, one would expect an insoluble precipitate of cupric hydroxide to be thrown down. Instead, however, a deep blue transparent solution results. Such solutions have oxidizing properties and under the action of many substances capable of undergoing oxidation, such as aldehydes and many sugars, produce either a yellow precipitate of cuprous hydroxide CuOH or a red precipitate of cuprous oxide Cu_2O . In the laboratory the identification of reducing agents may be effected by what is known as *Fehling's solution*, which is prepared as follows: 34.6 g of blue vitriol are dissolved in 1 litre of water in one flask, while 177 g of Rochelle salts and 60 g of sodium hydroxide are dissolved in 1 litre of water in another flask. The two solutions are mixed directly before use. Since Fehling's reagent cannot be kept for a long time, it is prepared in small quantities for every individual experiment.

The laevo acid has not been found as a natural product; it was first prepared by Pasteur from racemic acid.

Mesotartaric acid is formed, together with racemic acid, when D-tartaric acid is boiled for several hours with a large excess of sodium hydroxide solution. Its potassium hydrogen salt, unlike the potassium hydrogen salts of the other tartaric acids, is readily soluble in cold water.

Mesotartaric acid melts at 140° , i.e., at a much lower temperature than the other tartaric acids.

*Racemic acid** can be prepared by mixing solutions of D- and L-tartaric acids. If the solutions are concentrated, the mixing is attended by the generation of heat, the less soluble racemic acid being precipitated in the form of crystals.

Unlike the optically active tartaric acids, which crystallize without water, racemic acid crystallizes as a hydrate $2\text{C}_4\text{H}_6\text{O}_6 \cdot \text{H}_2\text{O}$. The anhydrous acid melts at 204° . Its salts crystallize with a different

* Derived from the Latin *racemus* meaning grape-bunch.

amount of water and have a different solubility than the salts of the D- or L-acid. Calcium racemate, for instance, has such a low solubility that a solution of it grows turbid when selenitic water is added to it, which does not happen when selenitic water is added to solutions of the other tartaric acids.

All this confirms that racemic acid is not a mixture of the optically active acids, but a chemical compound of them.

Such optically inactive compounds have come to be known as *racemic substances*, or *racemates*, the name deriving from racemic acid, which was the first substance found to be optically inactive owing to the presence of equal quantities of isomers having an opposite rotatory action. Racemate vapours, solutions, and melts appear to be mixtures of the two optically active forms. If, for example, the molecular weight of racemic acid is determined according to the depression of the freezing point of its solution, the resulting value corresponds to the formula $C_4H_6O_6$. Similarly, the vapour tensions of racemic acid esters correspond to single and not double molecules. In the crystal lattice, on the other hand, X-ray analysis reveals the sites to be occupied by double molecules.

The Discovery of the Tartaric Acids. In 1769 Scheele isolated "ordinary", i.e., dextrorotatory, tartaric acid from tartar; racemic acid was discovered in 1822 as a by-product in the manufacture of that acid.

A thorough study of racemic acid was carried out in 1830 by Berzelius, who showed it to be an isomer of dextrorotatory tartaric acid. Racemic acid was found to differ from the dextro acid in a number of properties: unlike the dextro acid, it is optically inactive; its crystals do not have the asymmetrically situated sites typical of the dextro acid crystals.

At the end of the forties of the past century Pasteur, at that time a student of the Ecole normale in Paris, became interested in a piece of research by the German chemist Mitscherlich. Mitscherlich claimed that the sodium ammonium salt of dextrorotatory tartaric acid differed from the sodium ammonium salt of racemic acid in that a solution of the former rotated the plane of polarized light to the right, while a solution of the latter was optically inactive. All the other properties of these salts, including their crystalline form, were, according to Mitscherlich, identical. In Pasteur's opinion, the different behaviour of these salts in relation to polarized light could only be accounted for if the racemate crystals, unlike the tartrate crystals, did not have asymmetric sites. Pasteur therefore set about repeating Mitscherlich's experiments.

His investigations revealed that the tartrate crystals, unlike the racemate crystals, did have asymmetric sites. Moreover, when the racemate was crystallized from a solution at a temperature below 28° , crystals were formed that also had such sites, but some of the crystals were mirror images of others. Pasteur carefully separated the crystals of one-type from the other and found that their solutions had opposite rotatory effects. He mixed equal quantities of the two kinds of crystals and discovered that their solution was optically neutral.

From the dextrorotatory salt he obtained dextrorotatory acid, and from the laevorotatory salt he was the first to obtain laevorotatory tartaric acid. Finally, he mixed concentrated solutions of the right-hand and the left-hand acid, obtaining a precipitate of racemic acid.

Later Pasteur discovered mesotartaric acid and evolved methods for separating racemates into the optically active isomers.

148. Resolution of Racemic Substances into Optical Antipodes. Pasteur, working with racemic acid, evolved three methods for the resolution of racemates into optical antipodes.

1. *Spontaneous Resolution.* In crystallization, racemates sometimes separate into D- and L-isomers, which form enantiomorphous crystals that can be sorted mechanically on the basis of appearance.

An example of spontaneous resolution is furnished by the crystallization of sodium ammonium racemate:



At temperatures above 28° the racemate is crystallized from the solution; at temperatures below 28° D- and L-tartrate crystals are

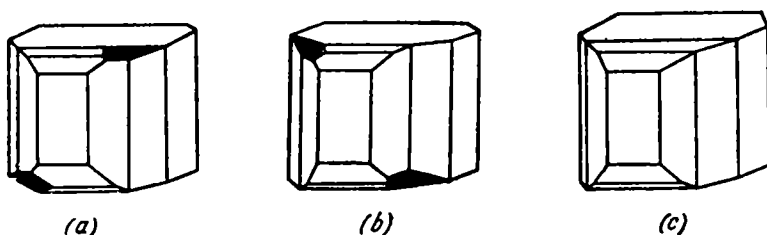


Fig. 52. Crystals of sodium ammonium salts of tartaric (a, b) and racemic (c) acids.

formed separately. The crystals differ, since they have dissymmetric faces (Fig. 52). They are called *enantiomorphous crystals* and can be separated manually. Their composition is expressed by the formula:



The sodium ammonium racemate crystals contain two molecules of water of crystallization.

2. *Biochemical Resolution.* This is based on the preference of microorganisms for one of the optical antipodes, usually for the one that occurs as a natural product in the animal or vegetable kingdom. For example, the common mould *Penicillium glaucum* consumes D-tartaric acid much faster and more readily than the L-acid. When the mould is therefore cultivated and grown in racemic acid solutions, only L-tartaric acid remains after a time.

3. *Chemical Resolution.* The resolution of racemates by this method is based on the different solubility of the salts of the antipodes of an optically active acid with an optically active base.

The resolution of racemic acid by means of cinchonine serves as an example of this. *Cinchonine* belongs to the alkaloid group and, with quinine, is found in the bark of the cinchona tree. It is a crystalline dextrorotatory substance with marked basic properties and combines with acids to form salts.

When racemic acid is treated with cinchonine, two salts are formed: a salt of D-tartaric acid with D-cinchonine and a salt of L-tartaric acid with D-cinchonine.

These salts are not optical antipodes, since the optical antipode of the salt of D-tartaric acid with D-cinchonine would be the salt of L-tartaric acid with L-cinchonine:

D-acid	L-acid	D-acid	L-acid
D-base	L-base	D-base	D-base
<u> </u>		<u> </u>	
optical antipodes		not optical antipodes	

Stereoisomers have the same properties only provided the sole difference in their configuration is a mirror image—object relationship between their molecules, i.e., provided they are optical antipodes. But since the salts obtained in this case are not optical antipodes, they must have different properties, specifically a different solubility. Indeed, the cinchonine-L-tartrate is less soluble in water than the cinchonine-D-tartrate; the two salts can therefore be separated by crystallization. By treating each of them with hydrochloric acid, we separate the cinchonine as a hydrochloride and obtain D-tartaric acid from one salt and L-tartaric acid from the other.

149. Asymmetric Synthesis. When chemical syntheses involving substances with symmetric molecules produce substances with an asymmetric carbon atom, the resulting substances are inactive compounds. However, by using optically active substances, it is possible in certain cases to obtain optically active substances from substances without an asymmetric carbon atom. To accomplish this, the initial substance is linked to an optically active substance, which is removed after a new asymmetric atom has been obtained by a chemical reaction. In this way it is possible to synthesize optically active lactic acid $\text{CH}_3\text{—CH(OH)—COOH}$ from pyroracemic acid $\text{CH}_3\text{—CO—COOH}$, in whose molecule there is no asymmetric atom. An ester is prepared from the pyroracemic acid and the natural laevorotatory alcohol borneol $\text{C}_{10}\text{H}_{17}\text{OH}$ (p. 518). By reduction the ester is converted into bornyl lactate. This gives rise to a new asymmetric atom in the molecule and produces two substances: an L-bornyl-L-lactate and an L-bornyl-D-lactate. Since these substances are not optical antipodes, the rates of their formation are not the same: more of the former than the latter is produced. Saponification of the reaction product therefore yields a slightly laevorotatory lactic acid.

Similar asymmetric syntheses can also be effected by means of enzymes, which are themselves active optically. When, for instance, a racemic ester of mandelic acid $\text{C}_6\text{H}_5\text{—CH(OH)—COOH}$ is hydrolyzed in the presence of the enzyme lipase, the D-modifica-

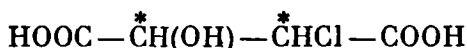
tion is hydrolyzed faster. Or if mandelonitrile $\text{C}_6\text{H}_5\text{—CH(OH)—CN}$ is prepared from benzaldehyde $\text{C}_6\text{H}_5\text{CHO}$ and HCN in the presence of emulsin—bitter almond enzyme—the resulting nitrile is an optically active modification. In the presence of enzymes it is thus possible to synthesize active molecules and to obtain an active substance from a racemate. Both processes probably take place when optically active natural products are formed. This would account for the fact that plants synthesize D-glucose and countless other optically active compounds from inactive substances (carbon dioxide and water), whereas laboratory syntheses with inactive initial substances invariably produce inactive substances. However, the original appearance of optically active organic substances in nature to this day remains a baffling problem.

Some scientists attribute it to photochemical processes. Indeed, when some racemates are exposed to right- or left-handed circularly polarized light, one of the antipodes is found to absorb more of the rays than the other and therefore decomposes faster. The substance surviving irradiation turns out to be optically active. By using light polarized circularly in the opposite direction, it is possible to obtain a substance in which the other antipode predominates. Several syntheses under the influence of circularly polarized ultraviolet have been carried out in the past two decades, yielding reaction products with an appreciable optical activity.

Asymmetric synthesis not involving products derived from living nature is called *absolute asymmetric synthesis*. As distinct from this, asymmetric synthesis with the participation only of agents derived from living nature is called *relative asymmetric synthesis*.

It was demonstrated recently by a group of Soviet chemists (A. Terentyev, Y. Klabunovsky, and V. Patrikeyev) that absolute asymmetric synthesis can be effected catalytically by means of catalytic substances deposited on crystals of dextro- and laevorotatory quartz, i.e., substances formed without the participation of living nature.

150. Stereoisomerism of Substances with Two or Several Asymmetric C-Atoms in Molecule. Diastereoisomers. In the tartaric acid molecule, the two asymmetric carbon atoms are equivalent. For a general consideration of the stereoisomerism of substances with several asymmetric atoms it is necessary for these atoms not to be identical. One such substance is chloromalic acid



One of the asymmetric carbon atoms in its molecule is linked to a hydroxyl, while the other is linked to chlorine. Each of them should therefore rotate the plane of polarized light to a different extent.

If we denote one of the asymmetric atoms by A and the other by B, and D- and L-rotation by plus and minus respectively, we get the following combinations for the four stereoisomers of chloromalic acid, which yield two different racemates:

1	2	3	4
+A	-A	+A	-A
+B	-B	-B	+B
first racemate		second racemate	

One of these racemates melts at 145° , the other, at 154° . Since in tartaric acid the asymmetric atoms are equivalent, modifications 3 and 4 are identical for it and constitute one and the same substance rendered inactive by internal compensation, mesotartaric acid.

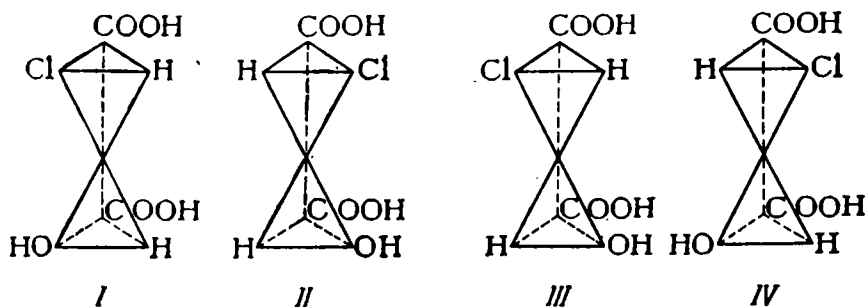


Fig. 53. Stereoisomerism of chloromalic acids:

I, II—optical antipodes; I, III—diastereoisomers; I, IV—diastereoisomers; II, III—diastereoisomers; II, IV—diastereoisomers, and III, IV—optical antipodes.

Fig. 53 gives the models of the four chloromalic acids. Modifications I and II, just as modifications III and IV, are optical antipodes, since the relationship in each pair is that of an object to its mirror image. Between modifications I and III, however, there is no such relationship. Modification I is not the mirror image of modification III. These acids are not optical antipodes and rotate the plane of polarized light through different angles. The same may be said of modifications II and IV. Such stereoisomers, which are not optical antipodes, are called *diastereoisomers*. The cinchonine D- and L-tartrates and the esters of the antipodes of an optically active acid with one of the modifications of an optically active alcohol are examples of diastereoisomeric substances.

Diastereoisomers differ not only in optical, but also in other physical properties, as well as in chemical properties. The differences become more marked with a rise in the number of asymmetric atoms in the molecule.

The molecule of chloromalic acid contains two asymmetric carbon atoms, and 4, i.e., 2^2 , stereoisomers are known for it. If a molecule

has three asymmetric atoms, the number of stereoisomers is 8, i.e., 2^3 , since the third asymmetric atom can combine with each of the four previous modifications in two different configurations:

1	2	3	4	5	6	7	8
+A	—A	+A	—A	+A	—A	—A	+A
+B	—B	+B	—B	—B	+B	+B	—B
+C	—C	—C	+C	+C	—C	+C	—C
first pair of antipodes		second pair of antipodes		third pair of antipodes		fourth pair of antipodes	

These eight stereoisomers form four pairs of optical antipodes. If there are four asymmetric atoms, the number of stereoisomers

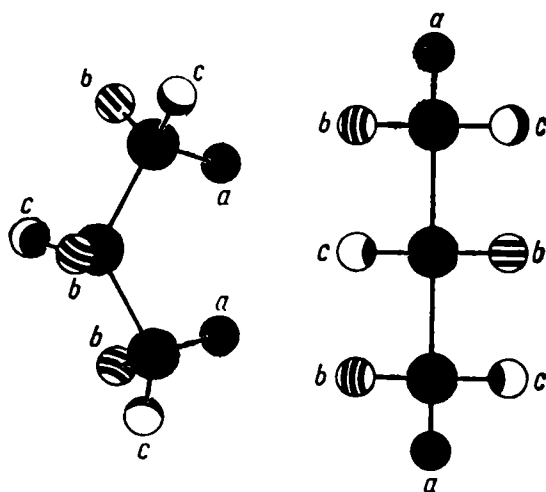


Fig. 54. Model and projection formula of molecule.

equals 2^4 , i.e., 16. Accordingly, if a molecule contains n non-equivalent asymmetric atoms, the number of possible stereoisomers is 2^n . Besides this, $\frac{2^n}{2}$, i.e., 2^{n-1} , racemates are possible.

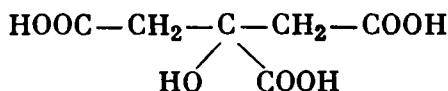
When molecules contain several asymmetric carbon atoms, they are not represented by spatial models; instead, projection formulas are used.

These are obtained in the following way.

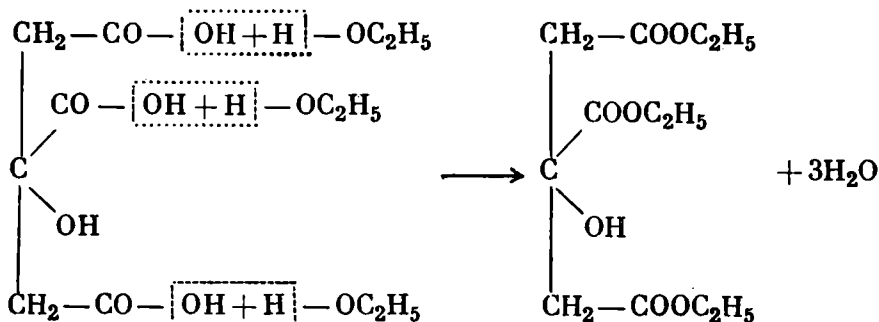
By revolving the atoms of the spatial model of the molecule about the single bonds, the carbon atoms of the chain are brought into a single plane, the chain forming an arc (Fig. 54, left). We then visualize the chain as if it were facing us with its bulging arc and stretch it out in a straight line in that plane, so that the substitutes linked to the carbon chain should be on the same side of the plane as before. The projection will then be in the plane of the paper (Fig. 54, right).

151. Citric Acid. Citric acid $C_6H_8O_7$ is contained in large quantities in plants: it occurs in lemons, gooseberries, raspberries, grape juice, etc. Considerable amounts are to be found in the leaves of rustic tobacco. It is prepared from the juice of unripe lemons (which contains 6-7% $C_6H_8O_7$) or by the fermentation of glucose under the influence of certain bacteria. Citric acid is known as a hydrate (with one molecule of water) and in the anhydrous state. The hydrate melts at about 70° ; the anhydrous acid, at 153° . Citric acid dissolves readily in water.

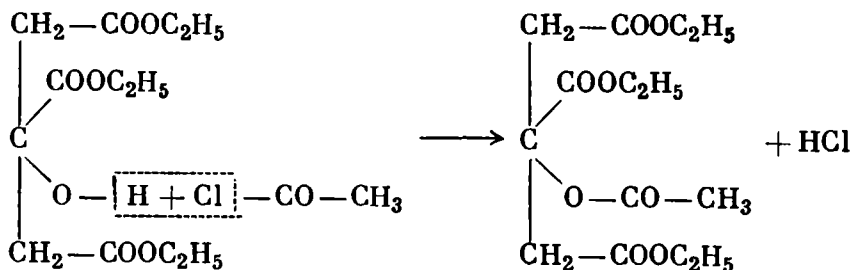
The structure of the acid is expressed by the formula:



Apart from the fact that its structure is confirmed by synthesis, the presence of three carboxyl groups in the acid is borne out by the formation of an ester with three molecules of an alcohol:



The presence of an alcohol hydroxyl in the citric acid molecule is corroborated by the fact that its ester reacts as an alcohol with the chloride of acetic acid, forming a new ester:

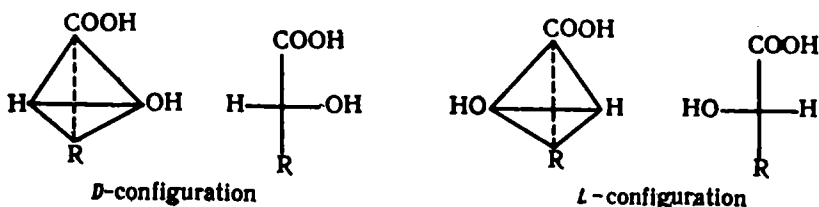


Among the citric acid salts, calcium citrate is of interest: it dissolves better in cold water than in hot.

Citric acid is used in the confectionary industry, in photography, and in blood conservation.

152. Stereoisomerism of α -Hydroxy Acids. The molecules of most hydroxy acids have an asymmetric carbon atom with a hydroxyl group attached to it. For the sake of uniformity the configurations

of these hydroxy acids are designated as follows:

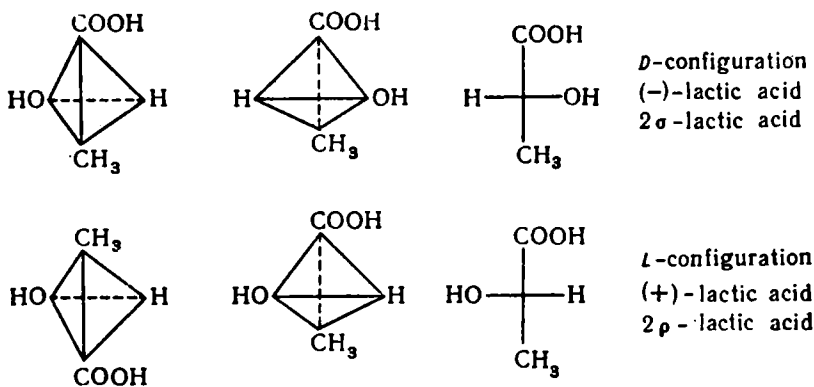


The *L*- α -hydroxy acids are thus 2σ -hydroxy acids, while the *D*- α -hydroxy acids are 2ρ -hydroxy acids.

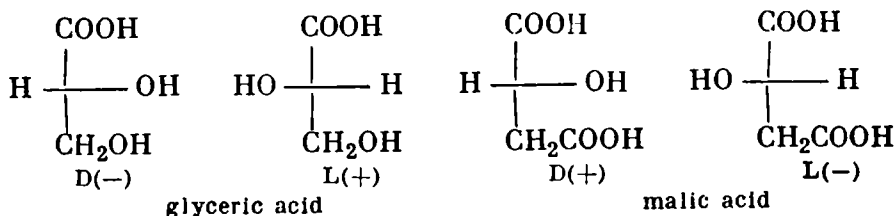
The designations ρ and σ , which we have been using up to now (p. 151), the designations *D* and *L*, and the rotation signs (+) and (−) are independent and can be used together, as, for example, in *D*(−) ρ -lactic acid. The difference in their use is that the designations *D* and *L* are in this case applied to the family of α -hydroxy acids, while the symbols ρ and σ are universal and have been introduced to give a graphic picture of the spatial structure of the molecules according to their names.

The symbols *D* and *L* in this case do not indicate the direction of rotation of the plane of polarization by these acids or their derivatives, but merely show the relative spatial position of the groups attached to the asymmetric carbon atom.

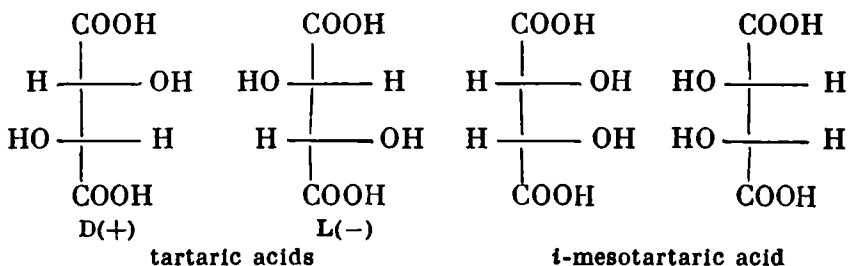
For lactic acid we thus have:



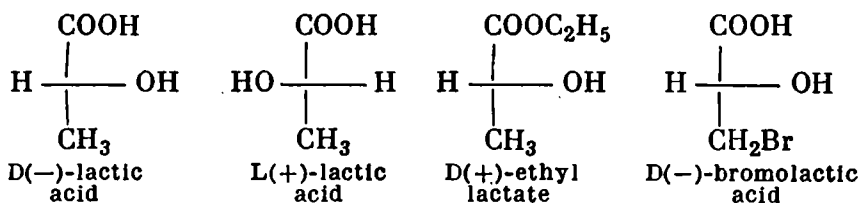
Attention should be given to the basic position of the spatial model, from which it is customary to derive the projection. It follows from the projection rule (p. 277) that the *horizontal* line (H—OH) in the spatial model represents a tetrahedral edge *in front* of the plane of the drawing:



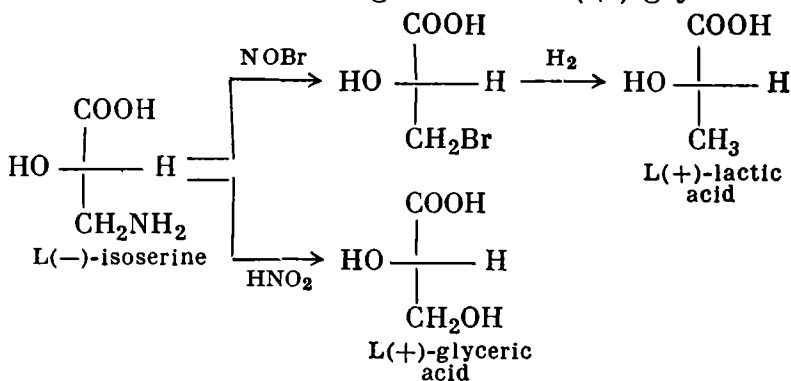
The structure of the tartaric acids in projection models is depicted as follows:



Evidently, the configuration and, hence, the symbol (D or L), but not the rotation sign (+ or -), will remain unchanged when we subject the initial substance to a chemical transformation that does not affect the bonds of the asymmetric carbon atom*:



It has been established by experimental methods that the molecules of (+)-lactic acid and (+)-glyceric acid have one and the same configuration; both acids can be derived (with due observance of the afore-mentioned provision) from (—)-isoserine, which, consequently, has the same L-configuration as (+)-glyceric acid:



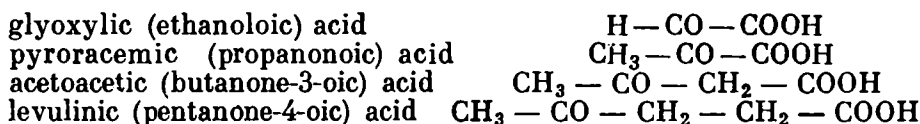
Since L(—)-isoserine is prepared from natural (—)-malic acid, it is obvious that malic acid has the same L-configuration.

* It was shown by P. Walden that in reactions involving the bonds of the asymmetric carbon atom there is often a mutual conversion of configurations (known as the "Walden inversion").

Aldehydo and Keto Acids

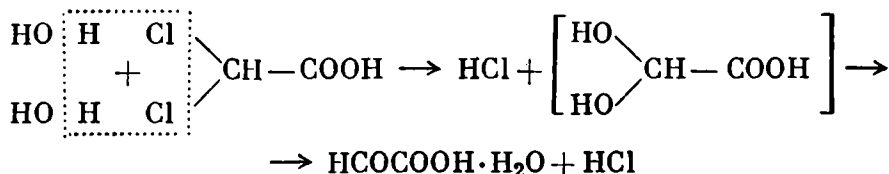
153. Structure of Aldehydo and Keto Acids. Some Representative Acids. The aldehydo and keto acids are compounds whose molecules contain a carboxyl group and an aldehyde or ketone group respectively.

The following are examples of such acids:

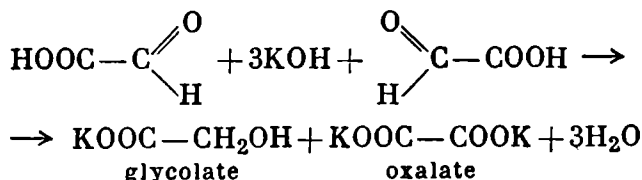


Pyroracemic acid is an α -keto acid; acetoacetic acid is a β -keto acid, and levulinic acid is a γ -keto acid.

Glyoxylic acid $\text{H}-\text{CO}-\text{COOH} \cdot \text{H}_2\text{O}$ occurs in unripe fruit, but disappears gradually as the fruit ripens. Since the molecule of glyoxylic acid is bound firmly with a molecule of water, the acid may be regarded as an aldehyde hydrate. The structure of the acid is established by its formation when dichloroacetic acid is boiled with water:

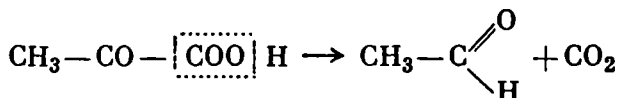


Under ordinary conditions glyoxylic acid is a syrupy liquid. When boiled with an alkali, it is converted into salts of glycolic acid and oxalic acid:

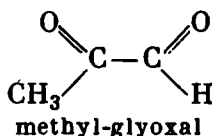
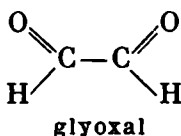


This involves the reduction of the aldehyde group of one acid molecule and the oxidation of the aldehyde group of another (the Cannizzaro reaction).

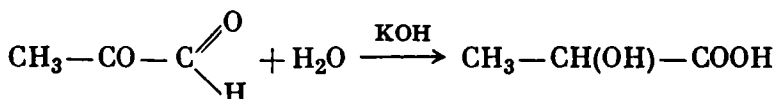
Pyroracemic acid $\text{CH}_3\text{—CO—COOH}$ can be prepared by the dry distillation of racemic acid. It is a liquid (m.p. 13.6° ; b.p. 165°) with an odour rather like that of acetic acid. Pyrорacemic acid is a by-product in alcoholic fermentation; the enzyme *carboxylase* (a component of yeast zymase) decomposes it into acetaldehyde and carbon dioxide:



The aldehyde corresponding to pyrорacemic acid is called *methyl-glyoxal*, since it can be looked upon as a methyl derivative of glyoxal:

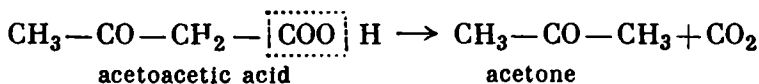


Methyl-glyoxal is an oily liquid with a pungent odour; it polymerizes readily. Subjected to the action of water in the presence of alkalis, it yields lactic acid:



The ketone group in this case is reduced, while the aldehyde group is oxidized.

Acetoacetic acid $\text{CH}_3\text{—CO—CH}_2\text{—COOH}$ is a syrupy liquid in the free state. Like all the other β -keto acids, it is unstable and is easily decomposed even by slight heating, with the evolution of carbon dioxide:

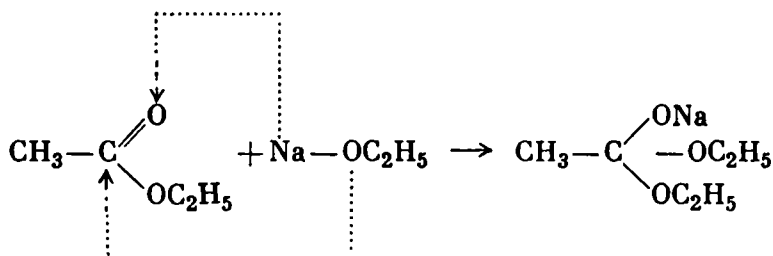


154. Acetoacetic Ester. Ethyl acetoacetate $\text{CH}_3\text{—CO—CH}_2\text{—COOC}_2\text{H}_5$, usually called acetoacetic ester, is the most important of the derivatives of the keto acids. It has many applications as a synthetic agent in organic chemistry and is of great theoretical interest.

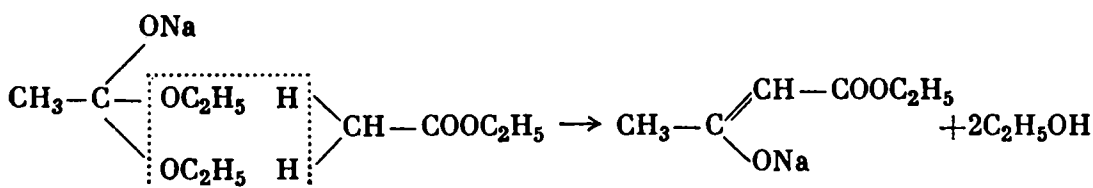
Acetoacetic ester is a liquid with a pleasant fruity odour; it boils at 180° , but undergoes slight decomposition; it is therefore purified by distillation at reduced pressure. It has a low solubility in water.

Preparation of Acetoacetic Ester. Acetoacetic ester is prepared by the action of sodium on ethyl acetate. There are several viewpoints concerning the mechanism of this reaction. According to one

of them (Claisen), the sodium alcoholate formed from the ethyl alcohol that is always present in negligible amounts in even very pure ester is added to an ester molecule:

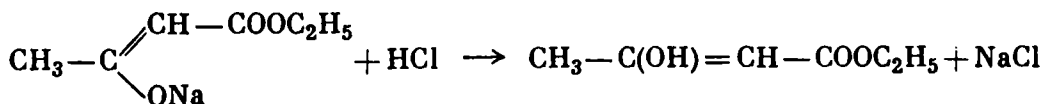


The addition product reacts with a second ester molecule, losing two alcohol molecules:

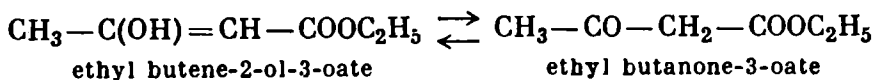


The alcohol again yields the alcoholate, which is again added to the ethyl acetate, etc.

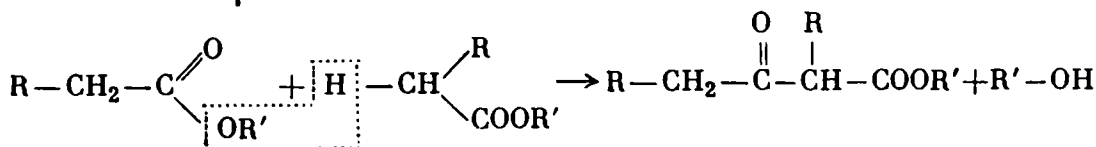
The reaction results in a sodium derivative of ethyl hydroxycrotonate, which, when subjected to the action of an acid, is released in the free state



and isomerizes into acetoacetic ester



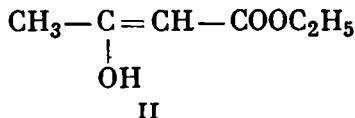
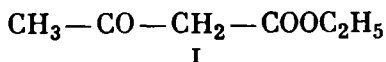
The esters of other acids containing a CH_2 group next to the carboxyl can also undergo this condensation. It is the hydrogen atoms in this CH_2 group that make possible the condensation with the formation of β -keto acid derivatives:



Compounds in which a doubly bound carbon atom (ene) has a hydroxyl group (ol) attached to it are called *enols*. This chemical structure has several distinctive features.

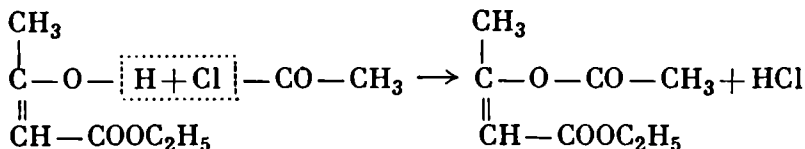
Structure of Acetoacetic Ester. The structure of "ordinary" acetoacetic ester was the subject of controversy among chemists for many

decades. Some regarded it as ethyl acetoacetate (I), while others considered it to be an ester of hydroxycrotonic acid (II):



The first formula classes ordinary acetoacetic ester among both esters and ketones; in accordance with the second formula it is both an ester and, at the same time, an unsaturated alcohol.

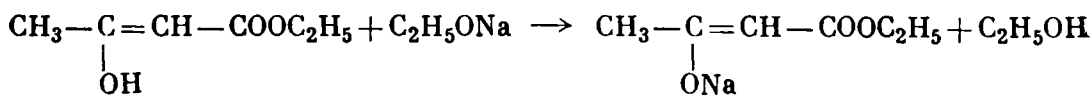
In some reactions ordinary acetoacetic ester behaves as an ethyl ester of acetoacetic acid. For example, like other ketones, it adds sodium hydrosulphite or hydrocyanic acid. But in other reactions it behaves as an ethyl ester of hydroxycrotonic acid. For instance, with acetyl chloride under certain conditions it forms a substance in which the acid radical is linked to oxygen:



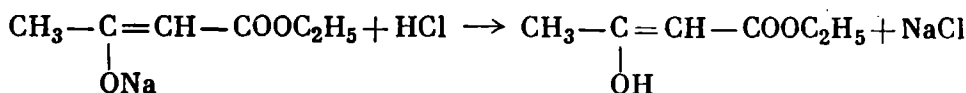
As an unsaturated compound, acetoacetic ester adds bromine, while as an alcohol with a hydroxyl attached to a doubly bound carbon atom it gives a deep violet colour with ferric chloride (which is a typical reaction of enols). In this way ordinary acetoacetic ester reacts both as a ketone and as an enol.

Numerous investigations have shown that ordinary acetoacetic ester is a mixture of two isomers: I (ketonic form) and II (enolic form). The two forms are in equilibrium, and, when this is disturbed, are quickly converted one into the other. When a few drops of ferric chloride are added to an aqueous solution of acetoacetic ester, the enol form of the isomer gives a deep violet colour. By then adding bromine drop by drop, it is possible to turn the enol form into a bromine derivative, the violet colour vanishing in the process. After a time, however, the violet colour reappears, since the disturbed equilibrium is restored and the keto form is partly converted into the enol form. The addition of bromine again turns the enol form into the bromine derivative. The entire quantity of acetoacetic ester can in this way be made to react in the enol form. On the other hand, by choosing a reagent that binds the keto form, such as NaHSO_3 , we can make the whole of the ester react as a ketone.

The action of sodium or sodium ethoxide on acetoacetic ester causes one atom of hydrogen in its molecule to be replaced by sodium. The resulting substance is sodio-acetoacetic ester:



If hydrochloric acid is now added to sodio-acetoacetic ester, the enol form of acetoacetic ester, which has a low solubility in water, may be isolated:



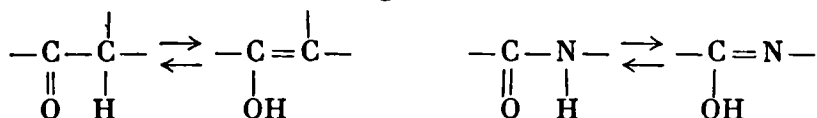
The rate of chemical reactions, including the rate of the isomeric conversion of the enol into the ketone, is reduced sharply by a drop in temperature. Therefore, by conducting the latter experiment in conditions of intense cooling, it is possible to obtain an almost pure enolic modification in the form of an oil that does not solidify at -78° . The enolic modification of acetoacetic ester, i.e., the ester of hydroxycrotonic acid, unlike the keto form, dissolves instantly in alkalis, adds bromine, and gives a colour with ferric chloride. On the other hand, by cooling a petroleum ether solution of ordinary acetoacetic ester in liquid air, it proved possible to obtain pure crystalline acetoacetic ester (m.p. 39°), which does not react with bromine and produces no coloration with FeCl_3 . Both modifications are at normal temperature converted to the ordinary acetoacetic ester, which is a mixture of 92.5% of the ketone and 7.5% of the enol.

155. Tautomerism. Acetoacetic ester thus exists in two isomeric forms, which are converted one into the other; it forms derivatives of both modifications.

This phenomenon of a substance existing in several isomeric modifications, which are easily converted one into another and are in a state of dynamic equilibrium, is called *tautomerism*. Tautomerism is observed very frequently in organic chemistry. The modifications experiencing these conversions are called *tautomers*, while their mutual transformations are called *tautomeric conversions*.

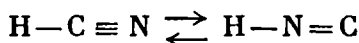
In the above case, where the tautomers are substances with a carbonyl group and enols (e.g., the isomeric forms of acetoacetic ester—p. 282 fol.), we observe *keto-enol tautomerism*.

The hydrogen atom in tautomeric conversions readily alters its position, with an attendant change in the character of the bonds, e.g.:



In the case of some tautomeric substances (e.g., acetoacetic ester or phenylnitromethane) it has been possible to isolate both isomers in pure form. The far more frequent cases of tautomerism, however, are those in which a substance yields derivatives of both isomeric

forms in chemical reactions, although the substance itself is known in only one modification. For instance, only one hydrocyanic acid is known, although it reacts in two tautomeric forms:

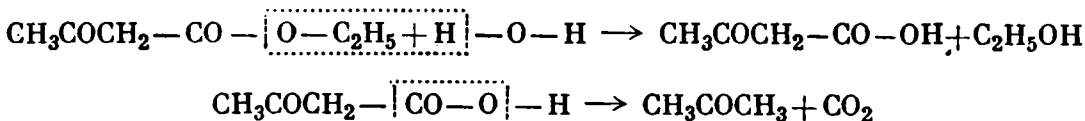


Both tautomeric forms of hydrocyanic acid cannot be isolated, owing to the exceedingly high rate of the tautomeric conversion.

It should be noted that as far back as 1876 Butlerov anticipated the discovery of the phenomenon that later came to be known as tautomerism. In a paper for the Academy of Sciences published in 1877 he wrote: "Most fluid substances are in a state of chemical equilibrium, with the number of molecules of one type being exceedingly great and the number of the other type or types being infinitely small.... There are, however, certain to be cases in which the quantity of one of the isomers is not minimal and the molecules of the two isomers are in constant 'competition' Evidently such a body should undergo chemical changes in the spirit of one or the other chemical group, depending on the nature of the reacting substances and the conditions of the experiment."

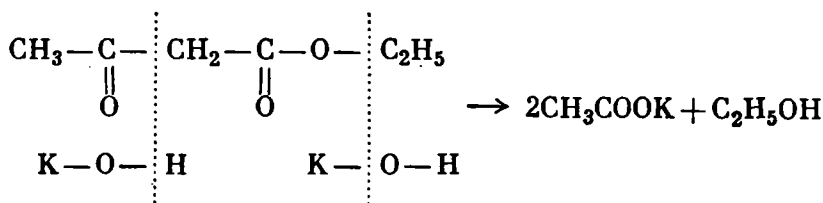
156. Syntheses Involving Acetoacetic Ester. Acetoacetic ester is split by the action of alkalis. The splitting proceeds differently, depending upon conditions.

1. The action of *dilute* alkalis (or acids) on acetoacetic ester causes its saponification, with the subsequent loss of CO_2 from the acetoacetic acid formed:



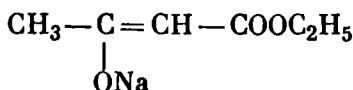
This is called the *ketone splitting*, or *ketone cleavage*, of acetoacetic ester. It results in the formation of carbon dioxide, alcohol, and acetone.

2. When acetoacetic ester is heated with *concentrated* alkalis, it undergoes *acid splitting*, or *acid cleavage*:

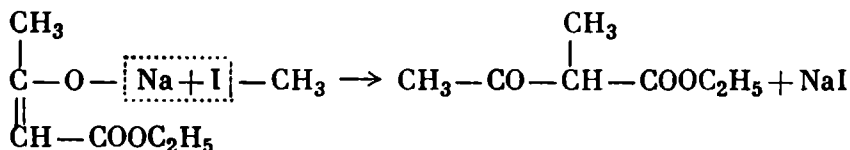


Syntheses of Ketones and Acids. As stated earlier (p. 283), the action of sodium or sodium ethoxide on acetoacetic ester pro-

duces sodio-acetoacetic ester:

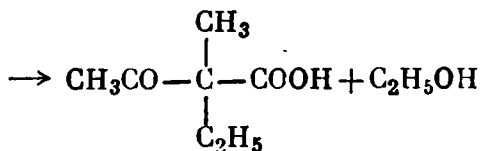
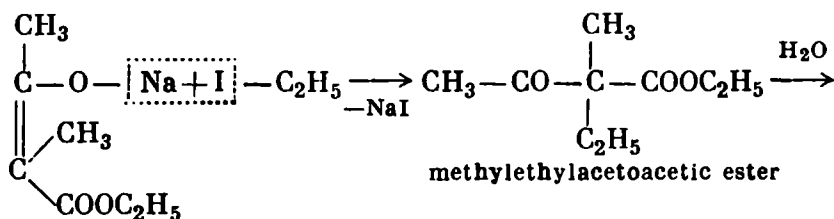
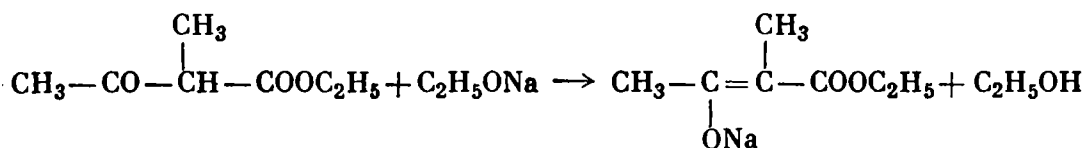


When this is subjected to the action of alkyl halides, the metal is replaced by the alkyl, which becomes linked to the carbon, and not the oxygen, despite the fact that in the ester the sodium was linked to the oxygen:



This phenomenon and many similar cases of the entry of radicals into positions other than those formerly occupied by the metal have been described by Nesmeyanov as a "shifting of the reactive centre".

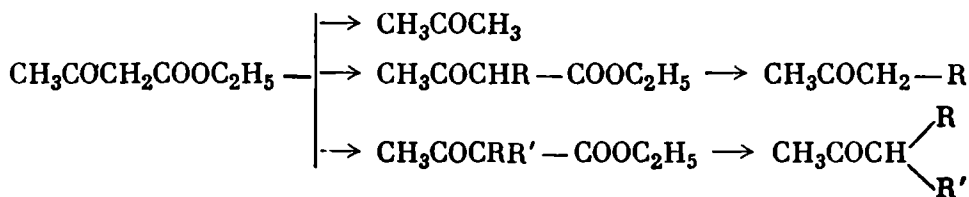
In the resulting ester one atom of hydrogen can be replaced by sodium, which in turn can be replaced by a radical:



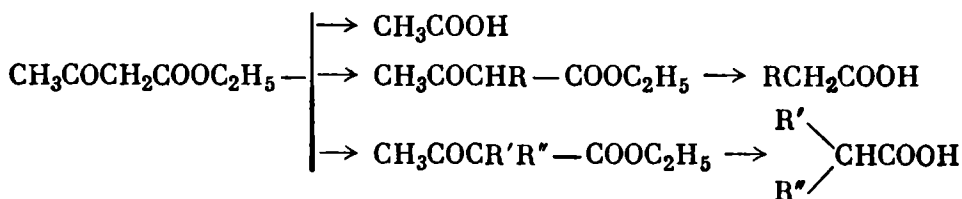
The result is a disubstituted derivative of acetoacetic ester.

Like acetoacetic ester itself, its mono- and disubstituted derivatives are capable of undergoing ketone and acid cleavage. The ester can in this way be used to synthesize ketones in which one of the radicals is methyl, while the other can have a normal or branched carbon chain.

The synthesis of ketones follows this pattern:



From acetoacetic ester and its mono- and disubstituted derivatives it is also possible to synthesize acids of normal and branched structure:



Carbohydrates

157. Classification of Carbohydrates. Carbohydrates occur in large quantities in plants and animals. They play a very important part in the processes which take place in living organisms. Glucose, or grape sugar $C_6H_{12}O_6$, cane or beet sugar $C_{12}H_{22}O_{11}$, starch and cellulose, both of which have the formula $(C_6H_{10}O_5)_x$, are examples of carbohydrates.

From the above formulas it is evident that these substances consist of carbon, hydrogen, and oxygen, the latter two elements being in the same proportion as in water, i.e., two atoms of hydrogen to every atom of oxygen. Their composition can therefore be expressed by the general formula $C_n(H_2O)_m$, which implies that they consist, as it were, of carbon and water. This accounts for their name, first suggested by the Russian chemist K. Schmidt (1822-94).

At present, however, we know both natural and synthetic substances in which this hydrogen-oxygen proportion is not observed, but which undoubtedly belong to the same class of substances as glucose and cellulose. Still, the formula $C_n(H_2O)_m$ does express the composition of the vast majority of the carbohydrates.

The carbohydrates may be divided into two groups:

1) the monosaccharides, or monoses, of which glucose is an example, and

2) the polysaccharides, or polyoses.

The latter group, in turn, may be divided into two groups:

a) the saccharoid polysaccharides (e.g., ordinary sugar), and

b) the non-saccharoid polysaccharides, of which starch and cellulose are examples.

The polysaccharide molecules consist of the residues of monosaccharide molecules; hydrolysis splits them up into simpler carbohydrates. The monosaccharides cannot be split up by hydrolysis.

MONOSACCHARIDES

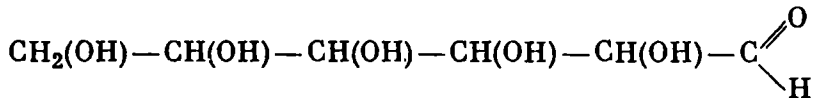
158. Structure of Monosaccharides. The structure of the monosaccharides will become clear from a study of glucose and fructose (fruit sugar). Both of them have a composition corresponding to the formula $C_6H_{12}O_6$.

An ester is known which is formed by one molecule of glucose and five molecules of acetic acid and which is prepared by treating glucose in the proper conditions with acetic anhydride. Consequently the glucose molecule has five hydroxyl groups. This was first established experimentally by A. Kolli* in 1869.

Glucose enters into certain reactions typical of aldehydes: for example, it produces a "silver mirror", whereas cautious oxidation causes it to add an oxygen atom with the formation of a monoacid. This indicates that the glucose molecule contains the aldehyde group.

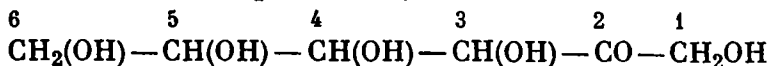
Upon vigorous reduction by hydrogen iodide, glucose is converted into 2-iodohexane $CH_3CH_2CH_2CH_2CHICH_3$. This shows that glucose has a normal carbon chain.

If we, therefore, take into consideration that one carbon atom can retain only a single hydroxyl, we can express the structure of glucose by the following formula:



According to this formula, glucose is both an aldehyde and an alcohol; it is an aldehydo-alcohol.

A molecule of fructose, like the glucose molecule, contains five hydroxyl groups, but, unlike glucose, fructose upon oxidation (by mercuric oxide in the presence of barium hydroxide) breaks up into two acids: trihydroxybutyric acid $CH_2(OH)-CH(OH)-CH(OH)-COOH$ and glycolic acid $CH_2(OH)-COOH$. This indicates that the fructose molecule contains a ketone group attached to the second carbon atom from the beginning of the chain; consequently the structure of fructose may be expressed by the formula:

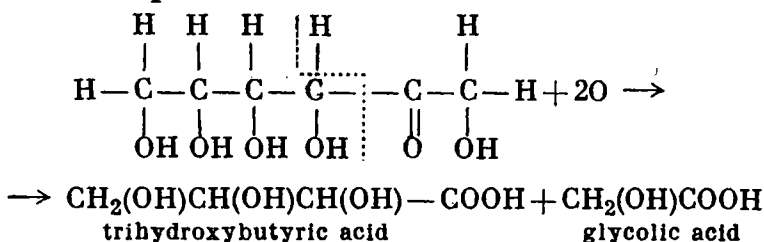


Fructose is both a ketone and a polyhydroxy alcohol; it is a keto-alcohol.

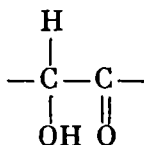
* Alexander Kolli (1840-1916) was a lecturer at Moscow University; from 1876 to 1903 he held the chair in chemistry at the Moscow Higher Technical School.

He was the author of several papers fundamental to the chemistry of the carbohydrates. He established that glucose contains five hydroxyls, proposed the cyclic structural formula for monosaccharides, performed the first synthesis of a disaccharide, etc.

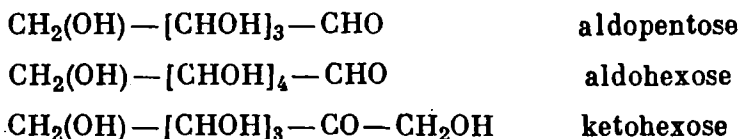
The oxidation of fructose by mercuric oxide in the presence of $\text{Ba}(\text{OH})_2$ can be depicted as follows:



The molecules of both glucose and fructose contain the group of atoms:

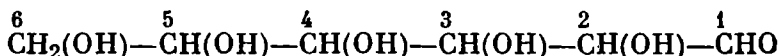


Monosaccharides containing the aldehyde group are called *aldoses*, while those containing the keto group are called *ketoses*. According to the number of oxygen atoms in the molecule it is customary to distinguish *bioses**, *trioses*, *tetroses*, *pentoses*, *hexoses*, *heptoses*, etc. Accordingly:



The naturally occurring monosaccharides are almost exclusively pentoses and hexoses. The overwhelming majority of the monosaccharides have normal chains of carbon atoms.

In accordance with the formula derived above

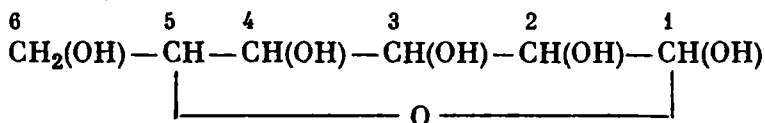


glucose is an aldehydo-alcohol. Several facts are, however, known that are not accounted for adequately by this formula. For instance, glucose does not exhibit certain aldehyde reactions: it does not produce a colour with fuchsin-sulphurous acid and does not react with chlorine or bromine in the absence of water (Kolli). When glucose is heated with anhydrous methyl alcohol containing a small amount of hydrogen chloride (as a catalyst), the hydrogen atom in one of the hydroxyl groups of glucose is replaced by a methyl group with the formation of methyl glucoside. Methyl glucoside does not exhibit any aldehyde reactions; it is easily hydrolyzed, breaking up into methyl alcohol and glucose. When methyl glucoside is treated with methyl iodide and silver oxide, the hydrogen atoms of the other four

* The term bioses is sometimes also used for disaccharides (p. 312 fol.).

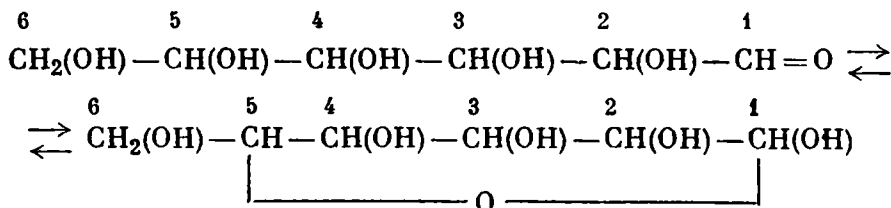
hydroxyl groups are likewise replaced with methyl groups; the resulting compound is called tetramethylmethyl glucoside. Upon hydrolysis, it first loses one methyl group, and the resulting 2,3,4,6-tetramethylglucose exhibits all the aldehyde reactions typical of glucose. One glucose hydroxyl is thus somewhat specific: once its hydrogen atom is replaced, the substance loses its aldehyde properties. This specific hydroxyl is called the *glucoside hydroxyl*.

These phenomena are well accounted for by a formula that attributes a cyclic (oxide) structure to glucose:

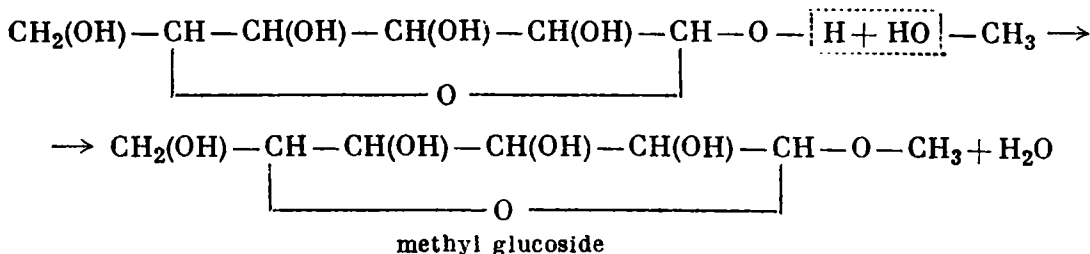


It is easy to see that the cyclic formula results from the aldehyde formula when the hydrogen atom from the hydroxyl of the fifth carbon atom is transferred to the first carbon atom's oxygen. This leaves the first carbon atom and the oxygen attached to the fifth carbon atom with free valencies, which saturate each other, so that a ring is formed consisting of five carbon atoms and one oxygen atom.

In a glucose solution there are molecules of the aldehyde modification and molecules of the oxide modification, i.e., tautomeric equilibrium:



When methyl glucoside is formed, the methyl group replaces the hydrogen atom of the hydroxyl attached to the first carbon atom, i.e., the hydrogen of the glucoside hydroxyl:



In the methyl glucoside molecule the first carbon atom has no hydroxyl group, and the molecule has no group that could become an aldehyde group. Methyl glucoside therefore does not exhibit aldehyde reactions. In the case of 2,3,4,6-tetramethylglucose, on the other hand, a tautomeric transformation into the aldehyde form

letters D and L were used to distinguish the dextrorotatory and laevorotatory modifications of optically active compounds. At present dextrorotation is designated by a plus sign (+) and laevorotation, by a minus sign (—), while the letters D and L serve to denote configuration types.

The ability of a substance to rotate the plane of polarization is one of its important characteristics; however, a comparison of the rotatory effects even of two highly similar compounds does not make it possible to establish whether they have the same or different configurations.

This is illustrated by the following example: sarcolactic acid rotates the plane of polarization to the right, whereas its salts and esters are laevorotatory, although they can be reconverted into sarcolactic acid, which certainly has the same configuration as its salts and esters. In many cases the sign of the rotation changes depending upon the solvent and even upon the concentration of the solution.

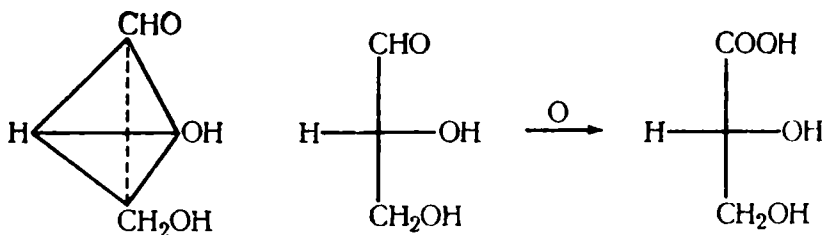
The initial substance adopted at present (at the suggestion of M. Rozanov in 1906) for comparing the configurations of optically active compounds is glyceraldehyde, known in the form of two antipodes:



Configuration (I) is assumed to correspond to dextrorotatory glyceraldehyde and is designated as D(+)-glyceraldehyde.

Substances whose configuration resembles that of D-glyceraldehyde are referred to the D-series, while substances of the L-series have a configuration like that of L-glyceraldehyde (II).

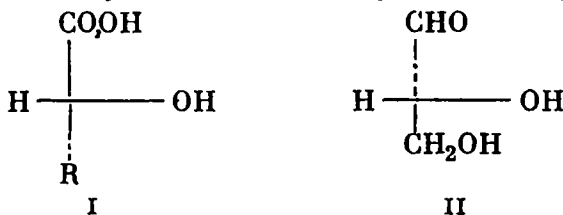
The oxidation of D(+)-glyceraldehyde yields D(—)-glyceric acid. This points to a similarity in the configuration of the two compounds:



The relative configurations of other α -hydroxy acids are determined in the same way.

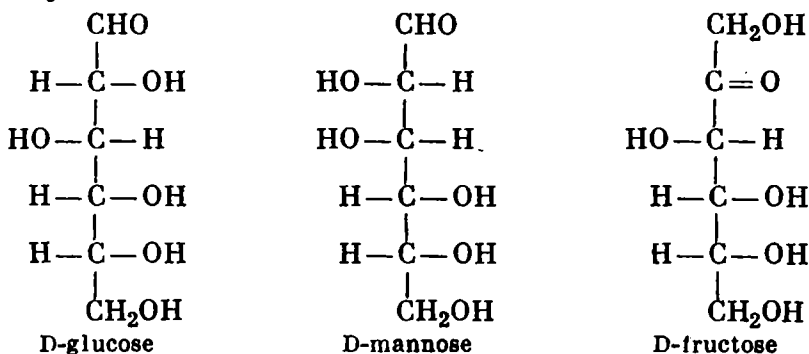
The family designations of (+)-glyceraldehyde and (—)-glyceric acid coincide, although glyceric acid is considered a D-hydroxy

acid according to the configuration of the asymmetric centre in α -position to the carboxyl, i.e., according to "key" (I):



The hydroxy aldehydes belong to the D family according to "key" (II), and this can give rise to misunderstandings (p. 350).

Whether a carbohydrate belongs to the D- or L-series is determined by the configuration of the asymmetric carbon atom furthest from the carbonyl:



Alpha- and Beta-Modifications of Monosaccharides. Sixteen stereoisomeric aldohexoses are possible, according to the aldehyde formula. In reality, however, there are more of them. A remarkable phenomenon is observed when a solution of D-glucose (ordinary natural glucose) is prepared: the specific rotation of the solution $[\alpha]_D = +113^\circ$ * diminishes gradually until it reaches the constant value $[\alpha]_D = +52^\circ$. This phenomenon is called *mutarotation*.

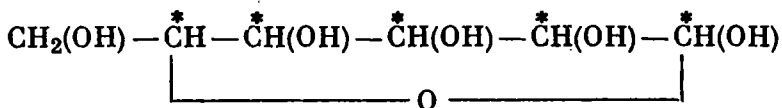
Consequently, glucose is transformed into some other substance, which has a smaller specific rotation. Investigations have shown that there are two stereoisomeric D-glucoses: α -D-glucose and β -D-glucose; the former rotates the plane of polarization through an angle six times greater than the latter does. Ordinary D-glucose is α -D-glucose.

In a solution or in the molten state the two modifications of D-glucose readily pass one into the other. The specific rotation of a newly-prepared solution of β -D-glucose $[\alpha]_D = +19^\circ$ thus rises with the passage of time. The increase continues until the specific rotation of the solution becomes equal to the specific rotation of a solution obtained by dissolving α -D-glucose. The solution therefore contains

* $[\alpha]_D$ indicates that the rotation has been determined for the yellow D line (wavelength 589 m μ).

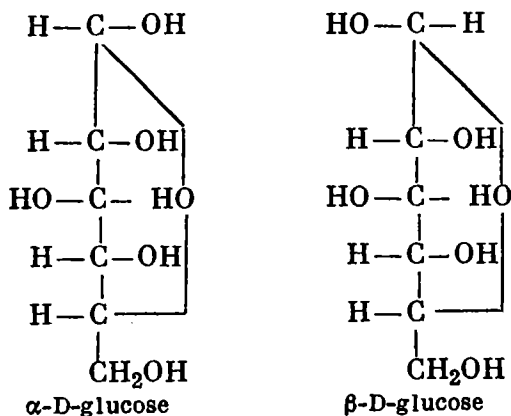
both forms of glucose, and a definite equilibrium sets in between them. Either form can be isolated from the solution, depending on the conditions of crystallization. Since α -D-glucose is less soluble in water than β -D-glucose is, it will be isolated from an aqueous solution. On the other hand, β -D-glucose will be crystallized from a solution of glucose in glacial acetic acid, if a small lump of β -D-glucose is introduced into the cooled solution. Derivatives of both modifications are known, e.g., α -methylglucoside and β -methylglucoside.

The existence of two modifications has, similarly, been established in the case of many other stereoisomers, possible according to the aldehyde formula. This phenomenon is accounted for excellently by the oxide formula:



According to this formula, the aldohexose molecule contains not four, but five asymmetric carbon atoms; therefore, there must be not sixteen, but thirty-two stereoisomers. In other words, for each of the stereoisomers corresponding to the aldehyde formula there can be two modifications: α - and β -forms. A comparison of the oxide and the aldehyde formula shows that according to the oxide formula the aldohexose molecule contains only one extra asymmetric carbon atom, namely, the first carbon atom. The difference between the molecules of the α -form and the β -form therefore boils down to a different spatial distribution of the groups attached to this carbon atom in the plane that forms the base of a tetrahedron for this atom.

To move mentally from the OH group via the H atom to the oxygen that bridges the ring we must travel clockwise in the molecule of one modification and counter-clockwise in the molecule of the other:



In the molecule of the β -modification the hydroxyl groups attached to the first and second carbon atoms are on different sides of the ring and the distance between them is greater than the distance between

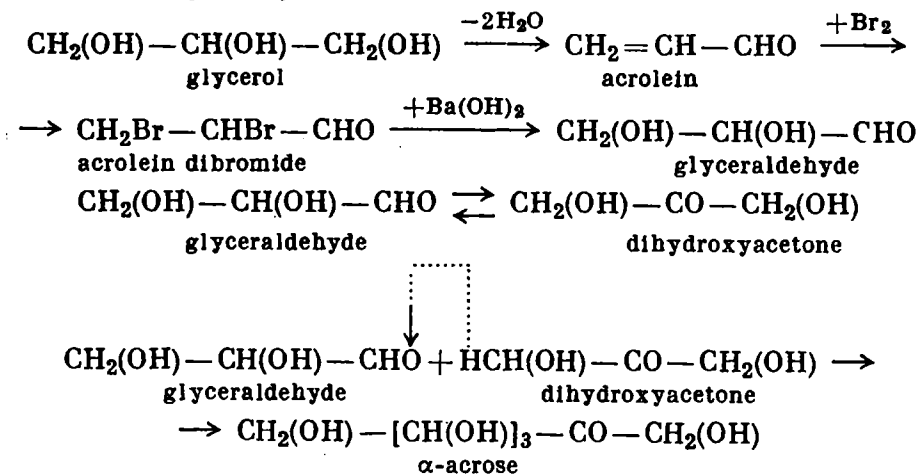
the same hydroxyl groups in the molecule of the α -modification. This accounts for the fact that a glucose solution contains more of the β -modification, which has a lower store of energy.

160. Natural Occurrence and Preparation of Monosaccharides. The monosaccharides are widespread in nature, both in the free state and in bound form. They are formed by the hydrolysis of polysaccharides, tanning matter of the tannin type, and some complex proteins (nucleoproteins and glucoproteins). The hydrolysis of starch, for example, yields glucose:



The first synthesis of a saccharoid substance was accomplished by Butlerov in 1861. By heating formaldehyde with lime cream he obtained a light yellow sweet syrup, which he named *methylenitan*, by analogy to mannitan (the old name of mannite). The syrup exhibited the usual monose reactions. Subsequently α -acrose, i.e., racemic fructose, was isolated from it.

Alpha-acrose as an individual substance was synthesized by Emil Fischer* in 1887 from acrolein $CH_2=CH-CHO$; the addition of bromine to acrolein yielded a dibromide; the latter, when treated with baryta water, gave glyceraldehyde, which, with partial isomerization to dihydroxyacetone, was converted to α -acrose:

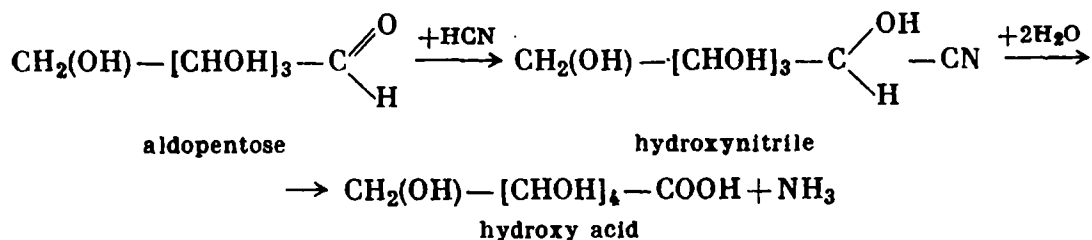


* Emil Fischer (1852-1919) was one of the most outstanding organic chemists. He studied and worked under Bayer. In 1892 he succeeded A. W. von Hofmann as professor of chemistry at the University of Berlin. He investigated the class of hydrazines and, specifically, phenylhydrazine, his work in carbohydrates being a sequel to these investigations. Fischer's work established that the carbohydrates are partly aldehydo-alcohols and partly keto-alcohols. Another series of his investigations was concerned with rosaniline and para-rosaniline. He also studied the derivatives of purine and advanced an original explanation, from stereochemical positions, of the action of ferments and the process of fermentation. The most important of all of Fischer's work was his study of protein substances, which marked the first concrete step towards the synthesis of proteins.

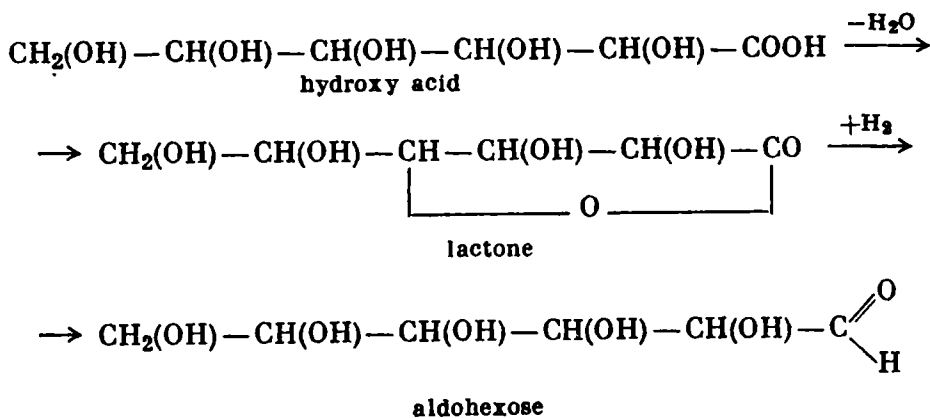
Fischer's across turned out to be a mixture of many sugars; glucose, mannose, and fructose were found to be contained in it. As Fischer put it, "glycerol proved to be the gates through which we advanced to the synthesis of natural saccharoid substances".

Monosaccharides with a large number of carbon atoms can be prepared by cyanohydrine synthesis from aldoses with fewer carbon atoms. The pentose-to-hexose conversion is an example of this.

The addition of hydrocyanic acid to aldopentose yields hydroxynitrile, which upon hydrolysis gives a hydroxy monocarboxylic acid:



The hydroxy acid is converted into a lactone, which upon reduction by sodium amalgam yields an aldohexose:

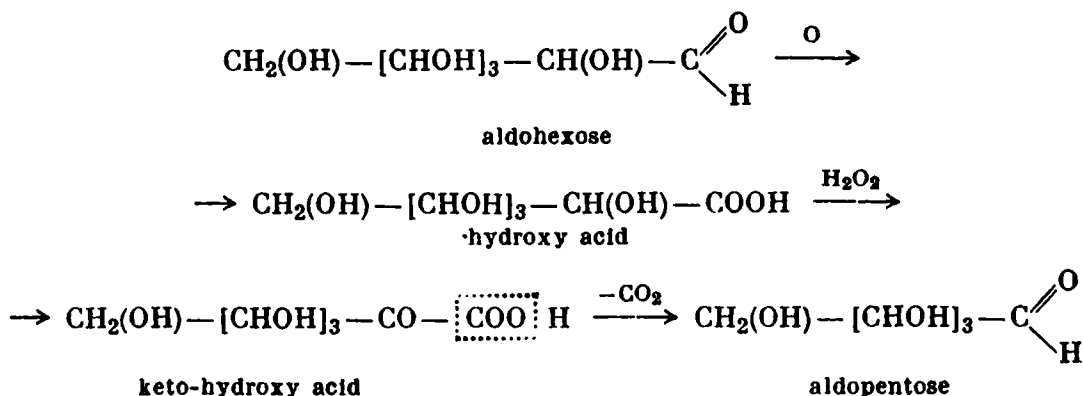


The heptoses $C_7H_{14}O_7$, the octoses $C_8H_{16}O_8$, the nonoses $C_9H_{18}O_9$, and even the decoses $C_{10}H_{20}O_{10}$ were prepared in this way.

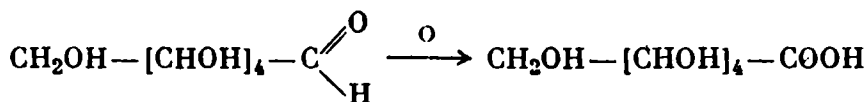
Monosaccharides with fewer carbon atoms can be prepared from monosaccharides with a greater number of carbon atoms by the Ruff method. The aldose is converted by oxidation into a hydroxy monocarboxylic acid, and its calcium salt is oxidized by H_2O_2 in the presence of ferric salts.

A keto-hydroxy acid is in all probability formed as an intermediate product, and this loses CO_2 to become an aldose with one carbon

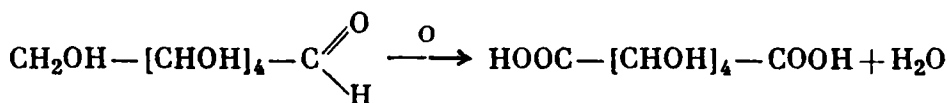
atom less than the initial aldose:



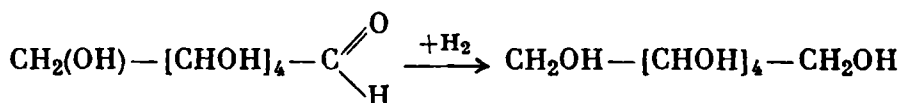
161. Properties of Monosaccharides. 1. Monosaccharides are easily oxidized; they reduce ammoniacal silver oxide and Fehling's solution. Gentle oxidation of aldoses yields hydroxy monocarboxylic acids with the same number of carbon atoms, so-called *onic acids*; glucose thus yields gluconic acid; mannose, mannonic acid, etc.



More vigorous oxidation (e.g., by concentrated HNO_3) produces hydroxy dicarboxylic acids; the hydroxy dicarboxylic acid resulting from the oxidation of glucose is called saccharic acid:



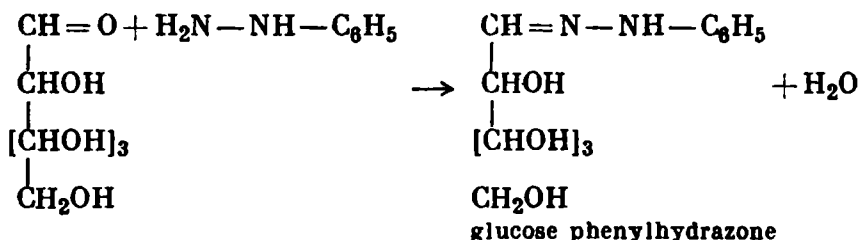
2. Reduction converts monosaccharides into polyhydroxy alcohols:



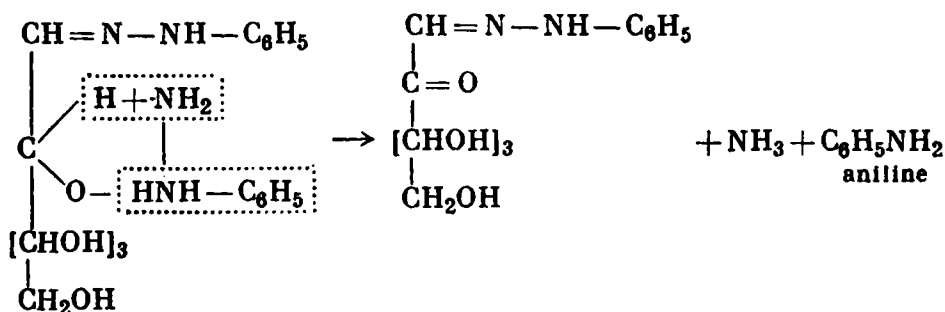
3. With phenylhydrazine monosaccharides, very characteristically, form *osazones*, or, to be more exact, *phenylosazones*.

To understand the reaction, let us consider the example of glucose.

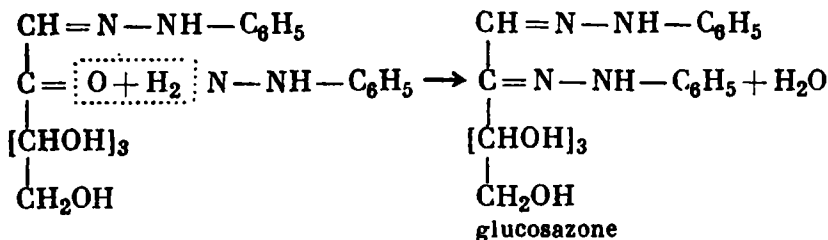
The phenylhydrazine reacts with the aldehyde group of glucose to form soluble phenylhydrazone:



When the phenylhydrazone is heated with excess phenylhydrazine, a second molecule of the latter enters into the reaction:

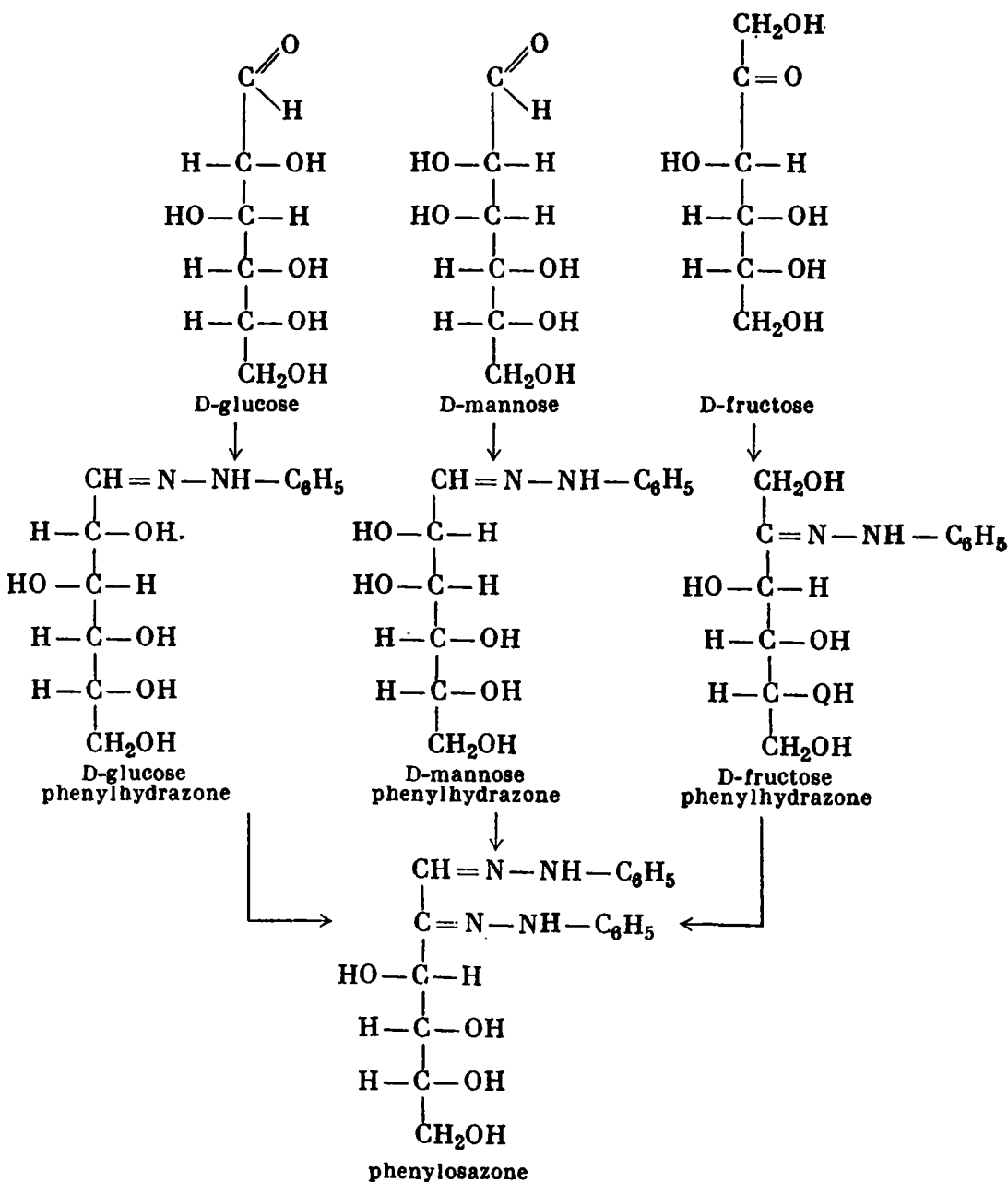


A molecule of phenylhydrazine in this case removes two atoms of hydrogen from an atom of carbon next to the carbonyl group; the molecule itself breaks up into ammonia and aniline, while in the phenylhydrazone molecule there arises a new carbonyl group. This group reacts with a third phenylhydrazine molecule, which produces glucosazone:



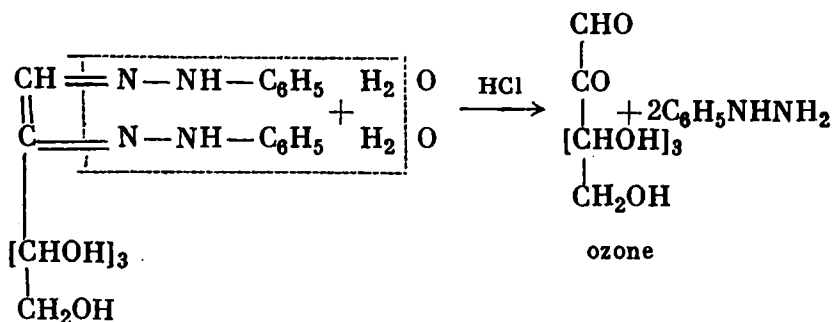
Phenyl-D-glucosazone has a low solubility in water. Its yellow needles melt at 204-205°. D-glucose, D-mannose, and D-fructose yield one and the same osazone. The carbonyl group is the first to react with phenylhydrazine. In the case of D-glucose and D-mannose the carbonyl group carbon is the first carbon atom; in the case of D-fructose it is the second. The osazones of D-glucose, D-mannose and D-fructose

are identical. Consequently: 1) the phenylhydrazine residues in osazone are linked with the first carbon atom and the second, and 2) the spatial distribution of the third, fourth, and fifth carbon atoms in the molecules of D-glucose, D-mannose, and D-fructose is the same:

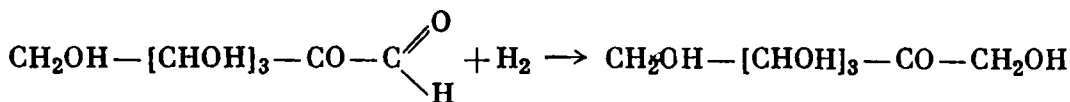


The configurations of D-glucose and D-mannose differ only in the spatial distribution of the atoms attached to the second carbon atom. Such aldoses are known as *epimers*.

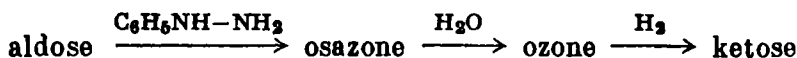
4. When osazones are heated gently with strong hydrochloric acid, they lose two phenylhydrazine molecules, forming *ozones*:



The ozones, in addition to hydroxyls, contain an aldehyde and a ketone group. When they are treated with zinc dust and acetic acid, the aldehyde group is reduced and this produces ketoses:



Via osazone and ozone, aldoses can thus be converted to ketoses:

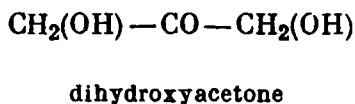
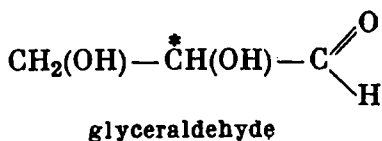


5. The action of dilute alkalis converts aldoses partly into their epimers and a corresponding ketose. For instance, D-glucose is partly converted into D-mannose and D-fructose. The action of concentrated alkalis, on the other hand, decomposes monosaccharides, the solution turning brown. Hexoses are decomposed by strong alkalis into lactic and other acids.

6. Like the alcohols, the monosaccharides, when treated with acid anhydrides, form esters. With alkalis and with the hydroxides of the alkaline earth metals they produce compounds of the alcoholate type. The methylation of monosaccharides was discussed earlier (p. 291).

7. For the fermentation of monosaccharides see pp. 310-12.

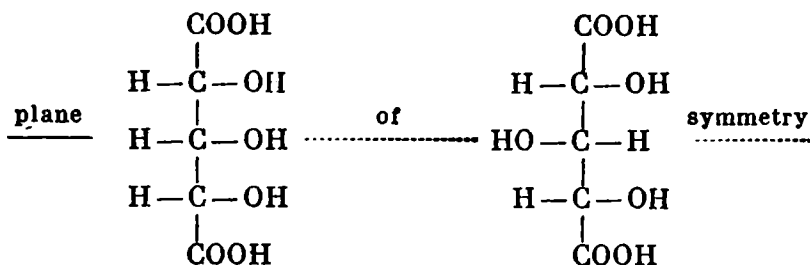
162. Trioses. The principal trioses are *glyceraldehyde* and *dihydroxyacetone*:



A mixture of the two trioses is formed if glycerol is oxidized carefully, say, by hydrogen peroxide in the presence of ferrous salts. The mixture is a syrupy liquid exhibiting typical monose reactions;

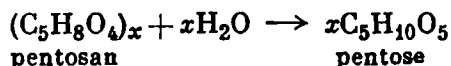
Alpha- and beta-modifications are possible for each of these eight stereoisomers.

All the aldopentoses can be oxidized to trihydroxyglutaric acids $\text{HOOC}-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{COOH}$. In accordance with the above-mentioned projection formulas, ribose and xylose yield optically inactive trihydroxyglutaric acids:

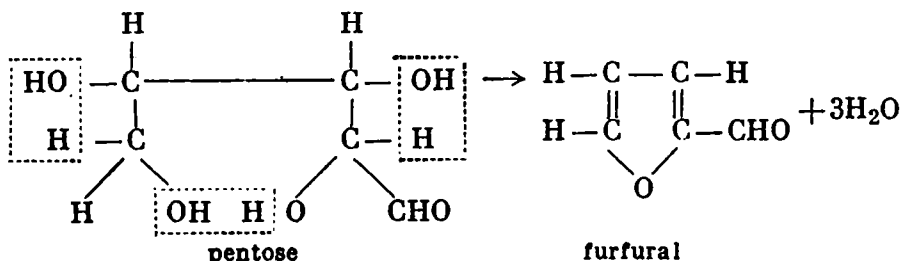


In the molecules of these acids the two asymmetric carbon atoms linked to the carboxyls have opposite configurations and there is mutual compensation. The molecules of these acids are symmetric. On the other hand, the trihydroxyglutaric acids formed by the oxidation of arabinose and lyxose have asymmetric molecules and are therefore optically active.

In nature the pentoses occur chiefly as the polysaccharides *pentosans* $(\text{C}_5\text{H}_8\text{O}_4)_x$; they are also found in pectin substances and in plant gums, such as gum arabic and cherry-tree gum (p. 325). There are also pentosans in wood (deciduous trees contain 22-27% pentosans), hay (10-15%), straw, seed hulls, sunflower seed hulls, etc. Hydrolysis causes pentosans to break up into pentoses:



Heating with acids converts pentose into a cyclic aldehyde called *furfural*. Each pentose molecule in this case loses three molecules of water:

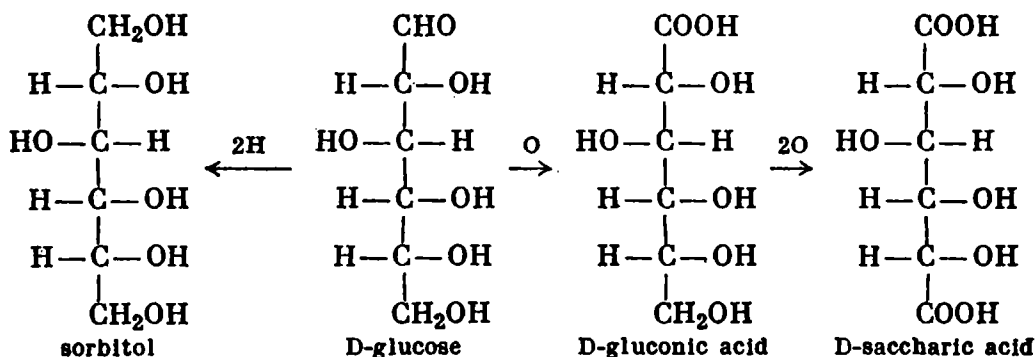


The presence of furfural may be detected by certain colour reactions. For example, with phloroglucinol (p. 425) and hydrochloric acid it gives a cherry-red colour, while with aniline salts it gives a red colour.

In this acid the hydroxyl is attached to the fourth carbon atom, and its oxidation could not yield trimethoxyglutaric acid.

Glucose crystallizes as a monohydrate. The anhydrous glucose melts at 146° and is readily soluble in water. Glucose is just about half as sweet as sugar.

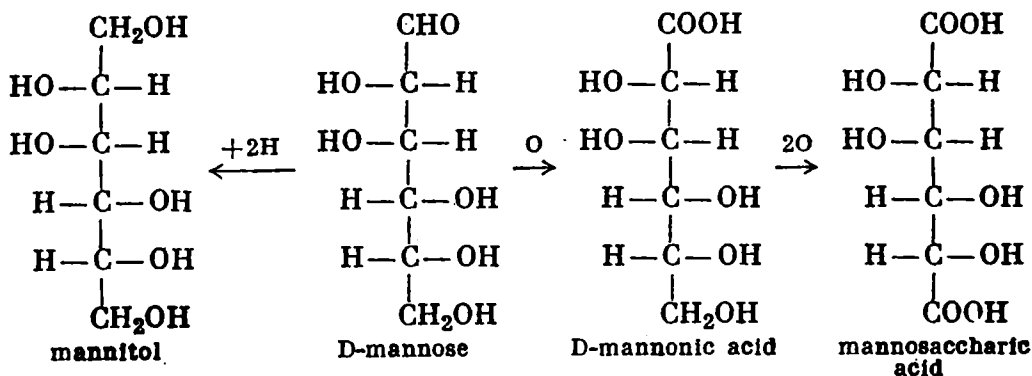
Upon oxidation, glucose at first yields *D-gluconic acid* and then *D-saccharic acid*. Reduction converts glucose into the hexahydroxy alcohol *sorbitol*:



Sorbitol occurs in mountain ash berries, in the juice of cherries, plums, apples, pears, etc. It melts at $110\text{--}111^{\circ}$ and has a sweet taste.

Glucose is used in the confectionery industry. In the cotton textile industry it serves as a reducing agent in dyeing and printing, serves to make mordants, etc.

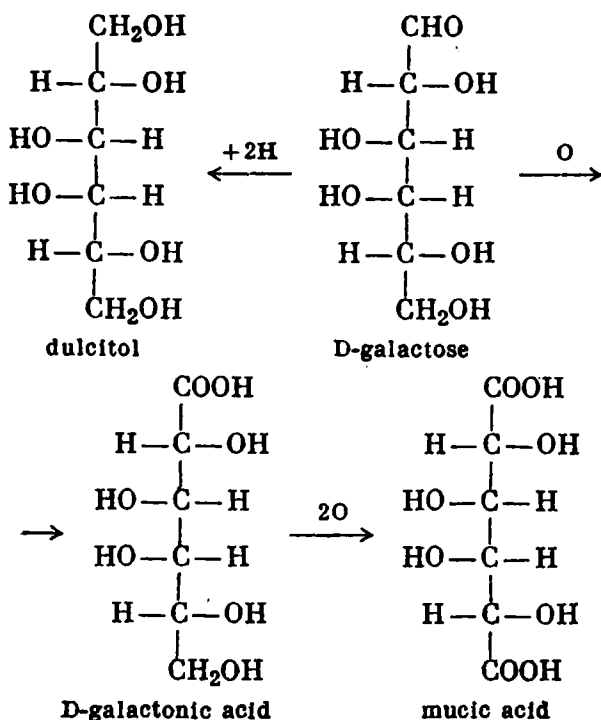
D-mannose occurs in nature primarily in the form of the polysaccharides known as mannans, which are contained in the seed case of the ivory nut, in the fruits of certain palms, in the grains of barley and wheat, in the roots of asparagus, chicory, etc. Mannose is a crystalline substance of sweet taste (m.p. 132°); it dissolves readily in water and exhibits mutarotation. Upon oxidation, it yields *D-mannonic acid* and *mannosaccharic acid*; upon reduction, it turns into the hexahydroxy alcohol *mannitol*:



Mannitol is contained in large quantities in what is known as manna, the dried exudate of certain southern and tropical plants. The

manna of the ash tree that grows in the Transcaucasus and Sicily contains up to 55% of mannitol. Certain White Sea algae also contain large amounts of the substance. D-mannitol is a crystalline substance of sweet taste; it melts at 165-166°.

D-galactose occurs in nature in the form of polysaccharides, e.g., milk sugar. It is a crystalline substance of sweet taste (m.p. 165°), it dissolves in water relatively well, and exhibits mutarotation. Upon oxidation, *D-galactose* yields *D-galactonic acid* and *mucic acid*. Upon reduction, it turns into the hexahydroxy alcohol *dulcitol*:

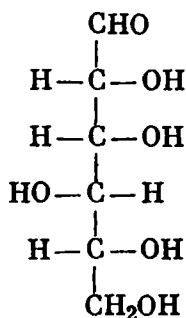


Mucic acid is a fine crystalline powder with a very low solubility in water; it is optically inactive.

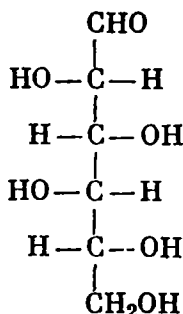
Dulcitol occurs in plants. It is a sweet crystalline substance (m.p. 188°), which is optically inactive.

D-fructose (fruit sugar) occurs with D-glucose in many sweet fruits; a mixture of equal amounts of D-fructose and D-glucose is the main ingredient (80%) of honey. The mixture is also an ingredient of cane sugar and inulin (p. 318). D-fructose usually forms crystals of the composition $2\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$; it is much sweeter than sugar and exhibits mutarotation.

Other important aldohexoses, in view of their relation to vitamin C, are the epimeric D-gulose and D-idose:

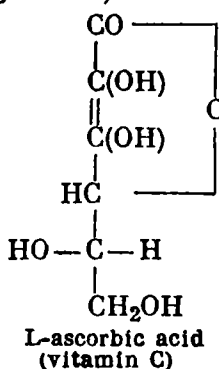
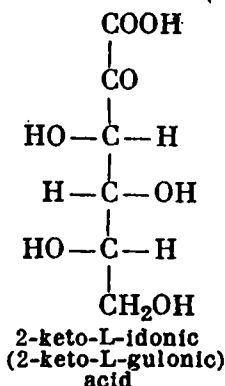


D-glucose



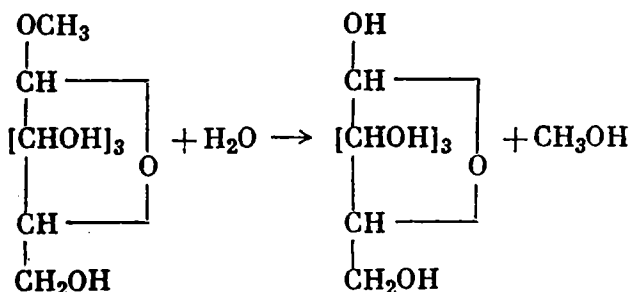
D-idose

Vitamin C, or L-ascorbic acid, is the enolic modification of the lactone of 2-keto-L-idonic (2-keto-L-gulonic) acid:



Vitamin C is a crystalline substance (m.p. 190°). It is optically active, is a strong reducing agent, and is very widespread in nature. It is present in fresh fruit, berries and vegetables; smaller quantities of it are to be found in raspberries and in butter. Black currants, lemons, oranges, and tomatoes are especially rich in vitamin C. A vitamin C deficiency in the diet causes scurvy. Ascorbic acid (vitamin C) is now produced on an industrial scale from D-glucose.

165. Glucosides. Glucosides are derivatives of carbohydrates, obtained by the replacement of the hydrogen atom in the glucoside hydroxyl by the residue of an *aglucone*, a non-carbohydrate substance. The action of acids or special enzymes breaks up glucosides into a carbohydrate and aglucone. Methylglucoside, for instance, is decomposed by hydrolysis into glucose and methyl alcohol:



The action of enzymes is specific. There are enzymes that split only α -glucosides, i.e., glucosides derived from α -forms of carbohydrates. Such enzymes are called *α -glucosidases*, e.g., yeast maltase. On the other hand, emulsin, an enzyme contained in bitter almonds, splits only glucosides of the β -series.

The hydrolysis of glucosides by enzymes is a reversible reaction. The enzyme that splits a glucoside also engenders its synthesis, i.e., gives rise to the equilibrium:



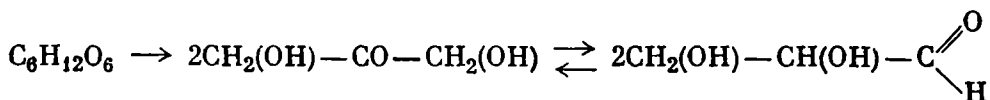
Glucosides are widespread in the plant world. They include the dye-stuffs of flowers and berries, as well as digitalis, salicin, and amygdalin.

166. Mechanism of Alcoholic Fermentation. In the course of many investigations by a number of scientists it was found that the breakdown of saccharoid substances to an alcohol and carbon dioxide is the result of several consecutive chemical reactions.

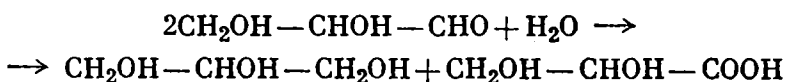
Several schemes have been suggested to account for the mechanism of alcoholic fermentation. The most credible appears to be the following.

1. Fermentation is preceded by the conversion of the glucose into phosphoric acid esters at the expense of the phosphates in the cell sap of yeast or other substances added during fermentation.

This is followed by the splitting up of the phosphate esters into dihydroxyacetone and glyceraldehyde, which are in dynamic (tautomeric) equilibrium*:



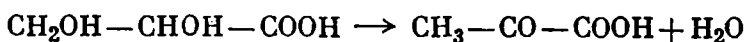
The glyceraldehyde subsequently undergoes the Cannizzaro reaction to form glycerol and glyceric acid:



If sodium fluoride is added to the liquid undergoing fermentation, the process of fermentation can be halted at this stage and glycerol and glyceric acid isolated from the liquid in the form of phosphate esters.

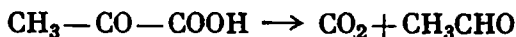
This phase may be regarded as initiating fermentation.

2. The glyceric acid is converted into pyroracemic acid:

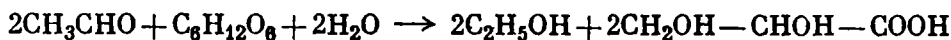


* For the sake of simplicity, reactions are given not for phosphate esters, but for corresponding simple saccharoid substances, acids, etc.

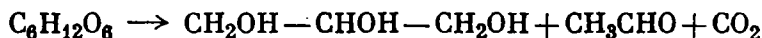
Under the influence of the enzyme carboxylase the pyrroacemic acid is decomposed into CO_2 and acetaldehyde:



3. The acetaldehyde is reduced by the glucose to ethyl alcohol, with the simultaneous formation of glyceric acid:



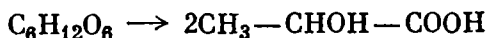
The process now becomes stationary: the glyceric acid again (via pyrroacemic acid) produces acetaldehyde and CO_2 , and so on. Fermentation in this way continues, by-passing the first phase. If Na_2SO_3 is added to the fermenting liquid, the last phase is short-circuited, the acetaldehyde being converted into hydrosulphite compound immune to the action of yeast enzyme. The main products of fermentation in this case are glycerol, acetaldehyde, and carbon dioxide:



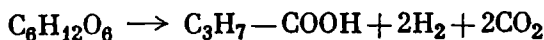
Yeast ferments D-glucose, D-mannose, D-fructose, and D-galactose. It has no effect, however, on the other hexoses; nor even on the antipodes of the above-mentioned carbohydrates, nor on the pentoses. In the D-glucose, D-mannose, and D-fructose molecules the spatial distribution of the hydrogen and the hydroxyl at the third, fourth, and fifth carbon atoms is the same, whereas in the D-galactose molecule it is different at one of the carbon atoms, namely the fourth; for this reason D-galactose is fermented by yeast with greater difficulty, while some types of yeast have no effect on it at all. To quote Fischer's apt comparison, the enzyme must fit the substance as a key fits a lock.

The alcoholic fermentation of hexoses is set up by yeast. Certain other microorganisms produce other types of fermentation.

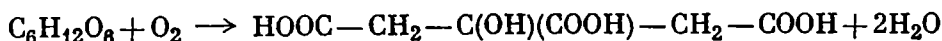
1. Lactic fermentation:



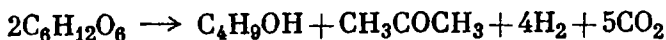
2. Buttery fermentation:



3. Citric fermentation:



4. Acetone-butyl alcohol fermentation:



Fermentation processes are very important in industry. The biochemical processes taking place under the influence of ferments are put to practical use in several types of production. In the organisms of the higher animals the processes of the biochemical decomposition and

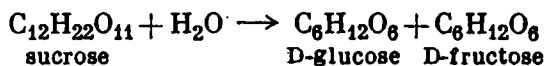
synthesis of monosaccharides proceed continuously. In muscular contraction the decomposition of carbohydrates gives rise to lactic acid and several other products.

LOW-MOLECULAR POLYSACCHARIDES (OLIGOSACCHARIDES)

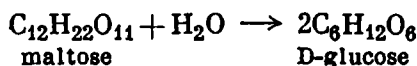
167. Properties and Structure of Disaccharides. *Polysaccharides are carbohydrates whose molecules, upon adding water, break up into molecules of monosaccharides or simpler polysaccharides. They are divided into two groups: saccharoid polysaccharides and non-saccharoid polysaccharides. The former group embraces the polysaccharides whose properties are similar to those of cane sugar. Most of them crystallize well, are soluble in water, have a sweet taste, and a definite molecular weight. The simplest of them are the disaccharides. The disaccharides are carbohydrates whose molecules, upon adding a molecule of water, break up into two monose molecules.*

The following are examples of disaccharides: 1) cane, or beet, sugar, known as sucrose; 2) malt sugar, or maltose; 3) milk sugar, or lactose, and 4) cellobiose. The composition of all the disaccharides is expressed by one and the same formula $C_{12}H_{22}O_{11}$.

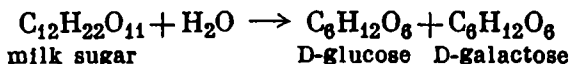
Sucrose is hydrolyzed into D-glucose and D-fructose:



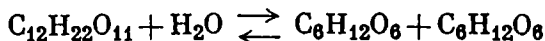
Maltose and cellobiose upon hydrolysis yield only D-glucose molecules:



Milk sugar is converted by hydrolysis into D-glucose and D-galactose:



The hydrolysis of disaccharides takes place under the influence of acids or enzymes, the action of the latter being selective. Invertase, one of the yeast enzymes, hydrolyzes sucrose, but has no effect on milk sugar; emulsin, on the other hand, breaks up milk sugar, but has no effect on sucrose. The hydrolysis of disaccharides is a reversible reaction:

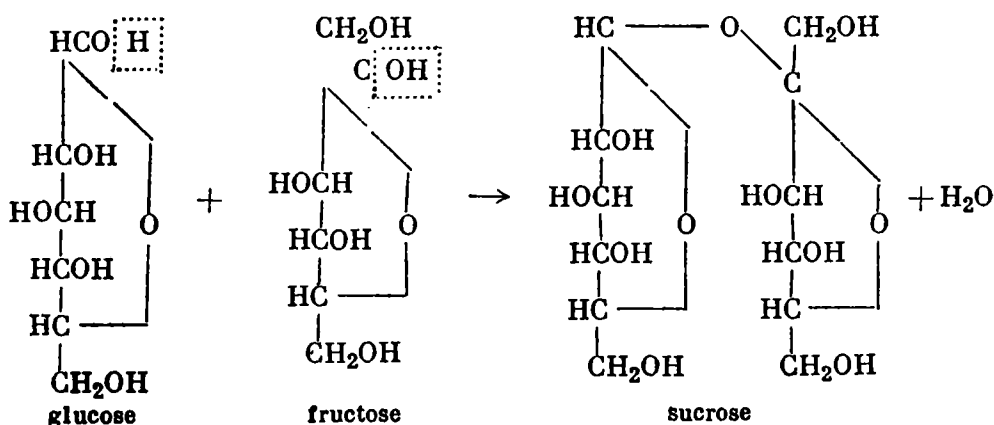


The enzyme that in the presence of excess water decomposes a disaccharide will in a concentrated solution engender its formation. For example, maltose is decomposed by yeast maltase into glucose, but by subjecting a concentrated glucose solution to the action of maltase it has been possible to obtain maltose. Cellobiose, when subjected

to the action of emulsin, yields glucose, but the treatment of concentrated glucose solutions with the very same emulsin produces cellobiose. Sucrose has not been produced synthetically as yet.

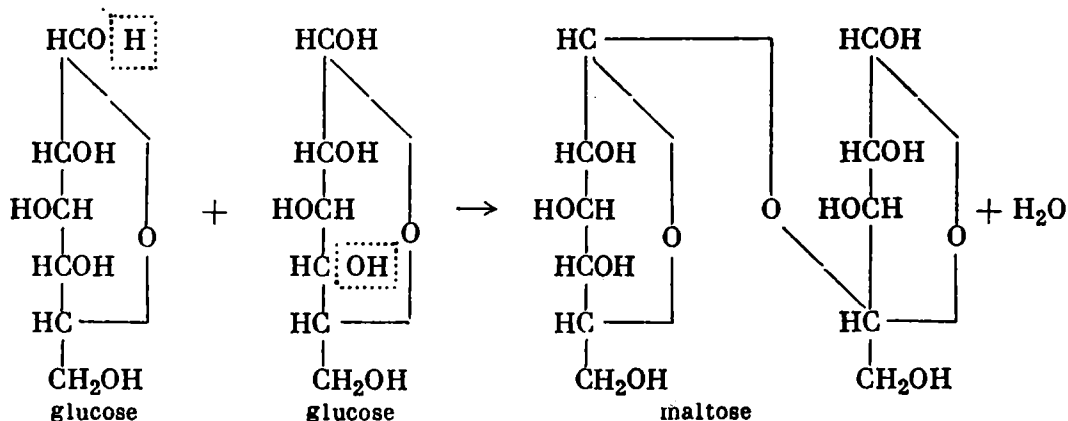
Some of the disaccharides reduce Fehling's solution, forming phenylhydrazones and osazones; consequently, their molecules contain a carbonyl or some group easily converted to a carbonyl. Other disaccharides do not contain this group, and they do not exhibit the above-mentioned reactions. The disaccharides of the first type include maltose, milk sugar, and cellobiose. The most important of the disaccharides of the second type is sucrose.

Sucrose. The sucrose molecule is converted by hydrolysis into a molecule of D-glucose and a molecule of D-fructose. Consequently, in the sucrose molecule the residues of the D-glucose and D-fructose molecules are linked by means of an oxygen atom; the formula of sucrose must therefore be derived from the formulas of glucose and fructose by the removal of the elements of water from hydroxyl groups. Since sucrose exhibits neither ketose nor aldose properties, does not reduce Fehling's solution, yields neither phenylhydrazone nor osazone, its molecule must be considered to have neither a carbonyl nor a group easily converted into a carbonyl. The elements of water are therefore removed from two glucoside hydroxyls, with the formation of a glucoside-glucoside bond, which accounts for the absence of active functional groups in the sucrose molecule:

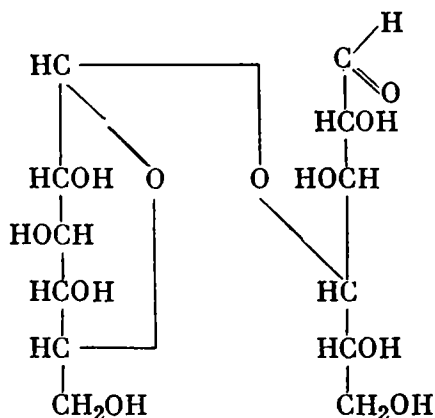


Maltose and Milk Sugar. Upon hydrolysis, maltose yields two molecules of D-glucose. This indicates that in it two D-glucose residues are linked by an oxygen atom. Oxidation causes maltose to add an oxygen atom, becoming a monocarboxylic acid. With phenylhydrazine it forms a phenylhydrazone. Consequently, its molecule contains an aldehyde group or a group easily converted into an aldehyde group. The elements of water must therefore be detached from the glucoside hydroxyl in the first molecule of glucose and from a non-glucoside hydroxyl in the second molecule. This hydroxyl, it has been

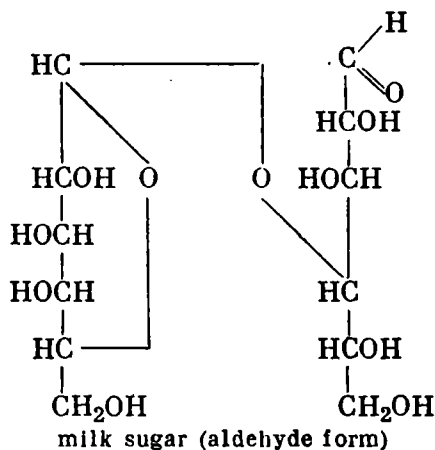
established, is the one at the fourth carbon atom. A glucoside-glucose bond is formed in this case:



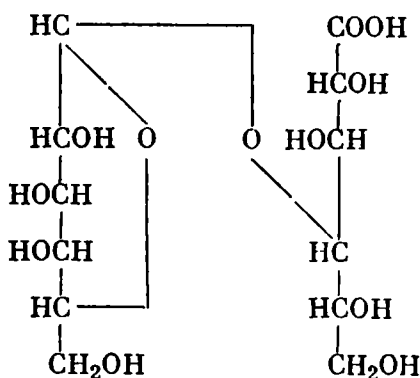
The presence of the glucoside hydroxyl has the effect that the maltose molecule can react in the aldehyde form:



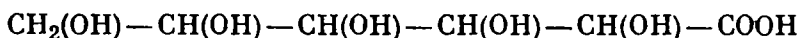
The structure of milk sugar is analogous to the structure of maltose with the sole difference that a molecule of D-galactose plays the part of a glucose molecule in it:



That the aldehyde group is retained by the glucose, and not the galactose, is confirmed by the fact that the mild oxidation of milk sugar yields lactobionic acid



which, upon hydrolysis, breaks up into a molecule of D-galactose and a molecule of D-gluconic acid



i.e., the acid produced by the oxidation of D-glucose.

In the molecules of milk sugar and maltose the residue of the glucose molecule retaining the group that turns into an aldehyde group can be in the form of either an α -D-glucose residue or a β -D-glucose residue. Milk sugar and maltose can therefore exist in α - and β -forms, which easily pass one into the other, while their solutions exhibit mutarotation. As for the first monosaccharide residue, it enters the disaccharide molecule in one definite form. In the maltose molecule, for instance, the α -D-glucose residue is the first residue.

Cellobiose. The structure of cellobiose differs from the structure of maltose in that the first residue in the cellobiose molecule is the β -D-glucose residue, whereas in the maltose molecule the α -D-glucose residue is the first. This is confirmed by the following. Maltose and cellobiose are derivatives of D-glucose, in whose molecule the hydrogen of the glucoside hydroxyl has been replaced by the residue of a second glucose molecule; they therefore have a glucoside structure. Glucosides of the α -series are split by maltase, while glucosides of the β -series are split by emulsin. Cellobiose is immune to maltase, but is hydrolyzed by emulsin. This places it in the β -series.

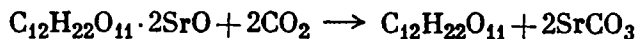
168. Sucrose. Sucrose, also called cane, or beet, sugar, is the ordinary sugar we all know. It is exceedingly widespread in the plant world. It plays an important part in the life of human beings, serving as a highly valuable element in nutrition and a factor making food tasty. Sucrose is readily assimilated by the human organism; the burning of 1 g of sucrose produces 4 Cal.

Sucrose forms colourless transparent crystals (m.p. 160°), but molten sucrose solidifies into an amorphous transparent mass called caramel. A solution of sucrose rotates the plane of polarization to the right. Hydrolysis breaks sucrose up into equimolecular quantities of D-glucose and D-fructose. A mixture of equal amounts of glucose and fructose is laevorotatory. The hydrolytic splitting of sucrose thus reverses the direction of the rotation of the plane of polarization. The process of the splitting of sucrose into glucose and fructose has for this reason come to be known as the *inversion* of sucrose.

Very large quantities of sucrose are contained in the stalks of sugar-cane and in sugar-beets. The extraction of sugar from sugar-cane dates back more than two and a half thousand years. The industrial production of sugar from sugar-beets began at the start of the past century. In Russia the first sugar refinery was built in 1802.

In the manufacture of sugar the beets are reduced to shreds and are then treated with hot water. The water extracts nearly all the sugar from the beets, while the remaining beet pulp is used for fodder. The juice obtained is of a dark colour and contains, in addition to the sugar, several admixtures (oxalic and phosphoric acids, proteins, dye-stuffs, etc.). After the removal of the admixtures (by lime treatment), the juice is filtered, evaporated in vacuum pans, and separated by centrifugal action from the crystals of sugar that have formed.

The mother-liquor remaining after the sucrose has been extracted is called *molasses*. It contains up to 50% of sugar and can be used either for further sugar-extraction or for the production of alcohol. To extract the sugar from molasses, it is boiled with a solution of $\text{Sr}(\text{OH})_2$. This produces the insoluble saccharate $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{SrO}$, which is filtered off and decomposed by carbon dioxide in an aqueous medium:



The juice obtained is subjected to the procedures described above.

White granulated sugar contains up to 99.9% of sucrose. To make the even purer cube sugar, the granulated sugar is dissolved in water, filtered through bone-char, and evaporated to a thick gruel. The latter is then poured into moulds, washed with pure syrup, and dried at reduced pressure.

The manufacture of sugar from the cane is similar to its manufacture from the beet.

169. Maltose. Lactose. Cellobiose. *Maltose* is formed as a result of the action of diastase, an enzyme in malt, upon starch, or as a result of the action of ptyalin, an enzyme of the saliva, upon starch. It is an intermediate product in the distilling and brewing industries.

Maltose crystallizes from water as a monohydrate. Its solution is dextrorotatory. It is approximately 40% less sweet than sucrose is.

Maltose is fermented by yeast, since the action of yeast maltase breaks it up into D-glucose.

Milk sugar (lactose) is contained in milk (4-5% in cow's milk; 5-8% in human milk). It is obtained from skim milk after the fat and casein have been removed.

Milk sugar crystallizes as a monohydrate. Its specific rotation is $+52^\circ$ (when mutarotation ends). It is about 70% less sweet than sucrose. Lactose is fermented by milk mould, which contains lactase; fermentation decomposes it into D-glucose and D-galactose. Wine lees and barm do not contain lactase and therefore do not ferment milk sugar. Lactose is an element in certain diets.

Cellobiose is obtained in the form of the ester cellobiose octoacetate when cellulose is treated with acetic anhydride and concentrated sulphuric acid. Cellobiose is a crystalline, very slightly sweet powder, which is soluble in water. It is dextrorotatory and exhibits mutarotation. Cellobiose reduces Fehling's solution.

HIGH-MOLECULAR POLYSACCHARIDES

The non-saccharoid polysaccharides are high-molecular compounds. Most of them are insoluble in water; some form only colloid solutions. Upon heating, they undergo decomposition without melting.

The principal representatives of the non-saccharoid polysaccharides are starch, cellulose, glycogen, and inulin.

170. Starch. Starch $(C_6H_{10}O_5)_x$ is contained in plants, serving as their food reserve material. It is one of the most important elements of nutrition of man and herbivorous animals. In the form of granules of different size and shape, starch is deposited primarily in the tubers and seeds of plants. Potato tubers, for example, contain about 20% of starch and 75% of water; wheat grains contain up to 70% of starch.

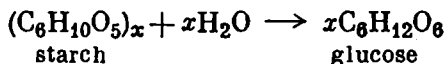
Starch is a white powder, insoluble in water. When heated with water, it forms a paste. With iodine, starch produces a blue colour, which disappears with heating, but reappears with cooling. Starch does not reduce Fehling's solution.

A starch granule consists of two different substances: *amylopectine* (the hull) and *amylose* (the interior) in a roughly 2 : 1 ratio. Amylopectine produces a paste; amylose forms a genuine colloid solution, which does not exhibit any properties of a paste. Amylose turns a pure blue with iodine; amylopectine, a reddish-violet. Amylose is a carbohydrate; amylopectine, a phosphate of another carbohydrate.

As it adds water, starch gradually decomposes into simpler carbohydrates. At first it turns into so-called *soluble starch**, which

* Starch that dissolves in hot water without forming a paste.

then decomposes into *dextrins*. Upon hydrolysis, the dextrins yield maltose, a molecule of which breaks up into two molecules of D-glucose. The end product of starch hydrolysis is thus D-glucose:



Starch is hydrolyzed when boiled with acids or by the action of enzymes, such as the *diastase* of malt or the *ptyalin* of saliva, which hydrolyze it to maltose.

A sample of the liquid, when starch paste is treated with acids or enzymes, gives first a violet, then a reddish-brown, and, finally, a yellow colour with iodine. The change in colour is due to the fact that the various decomposition products of starch give different colours with iodine. The violet and the reddish-brown are due to the dextrins, which are formed at first.

Maltose and glucose do not change their colour with iodine; nor do the simplest dextrins.

171. Dextrins. Dextrins are solids that are soluble in water. They are polysaccharides, but less complex than starch, and they reduce Fehling's solution. Commercially they are produced by heating starch to 180-200°. They can also be prepared by heating to 150° starch previously moistened with hydrochloric or with nitric acid.

Dextrins find many applications in industry as glue, as a thickener for dyes, in printing designs on calico, etc. The glistening crust of bread and the hard shining surface of starched linen consist of dextrins. Dextrins are also contained in the whole mass of baked bread. The process of baking is essentially one in which insoluble starch is converted into soluble and readily assimilated dextrins.

172. Glycogen. Inulin. *Glycogen* $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ serves as reserve food material in animal organisms, just as starch does in plants. It is deposited chiefly in the liver (up to 10%) and is also contained in the muscles. Glycogen is a white amorphous powder, which dissolves quite readily in hot water, producing a colloid solution that is coagulated by a negligible amount of salts. With iodine it gives a yellowish-red colour. A solution of glycogen is dextrorotatory. Acids and enzymes hydrolyze glycogen to D-glucose.

Inulin $(\text{C}_6\text{H}_{10}\text{O}_5)_x$, like starch, serves as a reserve food material of certain plants, but is not as widespread as starch. It occurs in the tubers of the dahlia (10-12%), in chicory roots (10%), in artichokes, narcissi, and many other plants.

Inulin is a white powder, which dissolves readily in hot water and does not change colour with iodine; its solution is dextrorotatory. Hydrolysis by acids and enzymes turns inulin into D-fructose.

173. Cellulose. Cellulose $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ is the chief constituent of plant cell walls. It usually occurs in plants not in the pure form, but

with what are called embedded substances (p. 325). Absorbent cotton, cotton textiles and linen, as well as high grades of filter paper consist for the most part of cellulose, somewhat altered in processing. The purest natural cellulose is the fibre of the cotton plant; it contains over 90% of cellulose and 6-8% of water. Cellulose accounts for about 50% of the wood of coniferous trees, but in deciduous trees its content is much lower.

Cellulose does not dissolve either in water, or in ether, or in alcohol; in ordinary conditions it is quite stable to the action of dilute acids, alkalis, and weak oxidizing agents.

Cellulose dissolves in Schweitzer's reagent (a dilute solution of cupric hydroxide in concentrated ammonia), in a hydrochloric solution of zinc chloride, and in concentrated sulphuric acid (see below).

Enormous quantities of cellulose in more or less pure form are prepared in the manufacture of paper. Up to the mid-nineteenth century paper was made almost exclusively from linen and cotton rags, which are nearly pure cellulose. With the expansion of book- and newspaper-publishing the production of paper from rags proved quite inadequate to meet the demand, and techniques were therefore evolved for obtaining cellulose from timber. At present the plainer sorts of paper are made from fir-timber. Paper of this kind, when stored, especially in the light, becomes brittle. The better sorts of paper are made from paper pulp, which is a mixture of wood pulp with more or less clean cellulose.

Several methods are used for the industrial manufacture of cellulose, the most widespread being the sulphite method. Under this method wood chips (mainly fir) are boiled at an increased pressure in huge 300 cu m and larger autoclaves with a solution of calcium bisulphite $\text{Ca}(\text{HSO}_3)_2$. The wood decomposes and partly passes into the solution; the cellulose in it survives in the form of a fibrous mass.

After the boiling the contents of the autoclave are pressed into a huge blow pit, a concrete reservoir with a floor of perforated plates. There the cellulose is separated from the solution and washed with water. The cellulose is then pressed, dried, and sent to the paper mills for further processing.

The solution separated in the blow pit is known as *sulphite liquor* and contains a considerable amount of saccharoid substances, which can be used for the manufacture of alcohol by fermentation. Such "hydrolytic" alcohol, used for industrial purposes, is made from raw materials that cannot be used for food production.

Apart from paper manufacture, considerable amounts of cellulose are utilized in the production of artificial fibre, plastics, lacquers, and gun-powders.

Hydrolysis of Cellulose. Cellulose, like starch, is hydrolyzed by acid solutions; its hydrolysis produces D-glucose:



The equation gives only the over-all result of hydrolysis. In actual fact, the hydrolysis of cellulose is a gradual process, which leads to the formation of simpler and simpler substances.

The action of strong sulphuric acid on cellulose for a short period of time turns it into *amyloid*, which gives a blue colour with iodine. This reaction is often used for the detection of cellulose. Chlorozinciodine, i.e., a solution of iodine and potassium iodide in a saturated solution of zinc chloride, is sometimes used for this purpose instead of sulphuric acid and iodine.

The formation of amyloid is used in the manufacture of parchment: unsized paper is placed for a few seconds in 80% sulphuric acid and then washed with water and an ammonia solution. A layer of amyloid is formed on the surface of the paper, which becomes impenetrable to water.

The action of mineral acids (hydrochloric, sulphuric) upon cellulose causes its partial hydrolization. The product is a brittle substance, which is easily ground to a powder, reduces Fehling's solution, and dissolves partly in alkalis. It is a mixture of unchanged cellulose and the products of its destruction and hydrolysis.

When cellulose impregnated with even dilute acid is dried, especially in a stream of hot air, it disintegrates readily into a powder. This property of cellulose is used to isolate wool from mixed yarn (cotton and wool).

More vigorous acid action causes the further hydrolysis of cellulose, with the formation of simpler and simpler polysaccharides. The ultimate product of the hydrolysis of cellulose is glucose.

In industry the culled wood of woodworking factories is used for the saccharification of cellulose. The culled wood is heated under pressure with an 0.1% solution of sulphuric acid; the syrup obtained is then converted into ethyl alcohol.

According to another method the cellulose is saccharified in the cold by the action of hydrochloric acid (relative density 1.21). The products of hydrolysis are then heated to remove the bulk of the hydrochloric acid and are neutralized with soda. The neutralized product is used as cattle feed.

Cellulose can also be broken down by microorganisms. Processes of this type are tremendously important in nature; it is in this manner that plant remains on the ground are disintegrated. One such process is the destruction of wooden buildings by dry rot, which oxidizes cellulose by means of the oxygen of the air to CO_2 and H_2O . An important process is the methane fermentation of cellulose, caused

by certain types of bacteria at the bottom of stagnant reservoirs; it takes place without access of air and yields methane, carbon dioxide, and fatty acids.

Cellulose and Alkalis. Although it comparatively readily succumbs to the action of acids, cellulose is highly resistant to alkalis.

Cold solutions of caustic alkalis cause cellulose to swell markedly and absorb alkali, forming chemical compounds with it. The compounds are called *alkalicelluloses*. An 18% solution of sodium hydroxide produces the molecular compound $[(C_6H_{10}O_5)_2 \cdot NaOH]_n$; it can be washed away from the sodium hydroxide solution by alcohol and then dried.

Alkalicellulose is easily decomposed by water and forms *cellulose hydrate*. In chemical composition cellulose hydrate does not differ from ordinary cellulose, but it is more hygroscopic; moreover, it gives up the bound water less readily. It also lends itself to dyeing readily and is less resistant to chemical action.

The alkali treatment of cotton textiles and yarn, and their subsequent washing with water, is called *mercerization*. The treatment of a fabric or yarn with an alkali causes it to shrink in size by about 20%; the fabric in this case becomes closer, the yarn, thicker. Their tear resistance increases considerably. This contraction in size and increase in strength do not change after the alkali has been washed away with water. If contraction is prevented mechanically, i.e., if the fabric or yarn is kept stretched during mercerization, the fibres acquire a high lustre and silky appearance.

Oxidation of Cellulose. The action of various oxidants (moist chlorine and its oxides, hydrogen peroxide, potassium permanganate) on cellulose causes its gradual oxidation with the formation of various types of oxycellulose. This is a mixture of unchanged cellulose with the products of its oxidation.

Oxycellulose contains substances with aldehyde and carboxyl groups; it reduces Fehling's solution, acquires a magenta colour under the influence of fuchsin-sulphurous acid, and often dissolves in alkalis.

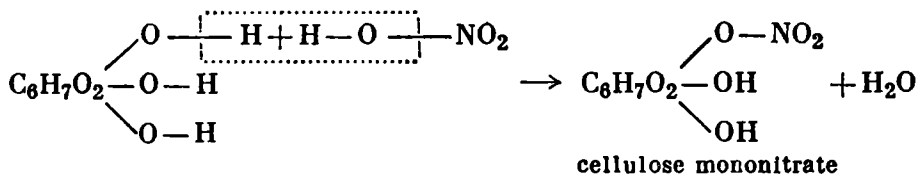
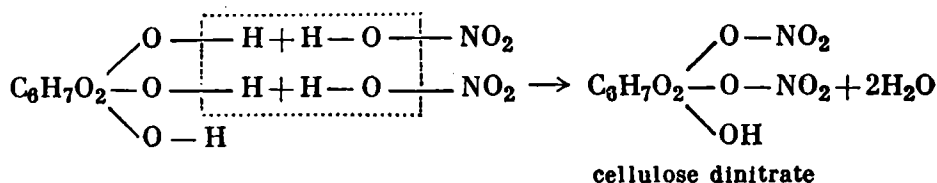
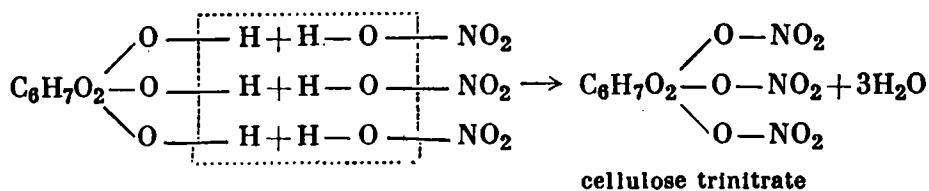
The oxygen of the air under ordinary conditions has practically no effect on cellulose, but an alkaline medium or a high temperature intensifies its effect. When cellulose is fused with alkalis, with the access of air, it is oxidized to oxalic acid.

174. Esters and Ethers of Cellulose. The cellulose molecule contains hydroxyl groups; according to its simplest formula $C_6H_{10}O_5$ there are three such groups, and the formula should therefore be written $C_6H_7O_2(OH)_3$.

Cellulose esters are known in which there are three monoacid radicals to each $C_6H_{10}O_5$ group. The most important of them are the

nitrates, acetates, and xanthates (esters of xanthogenic acid $C_2H_5OCS-SH$).

The cellulose nitrates are called *nitrocellulose*. They are prepared by treating cellulose with a mixture of nitric and sulphuric acids. For a single $C_6H_{10}O_5$ group the reaction can be expressed by the following equations:



Nitration* ordinarily produces a mixture of nitrates.

A mixture of the nitration products with a high nitrogen content (13-13.6%) is known as *gun-cotton*. Pressed into blocks it is used as an explosive in blasting. Pure gun-cotton cannot be used in fire-arms because it explodes too quickly. To reduce this speed the gun-cotton is treated with alcohol, ether, and other substances; the resulting plastic is made into ribbons and tubes of what is known as *smokeless powder*, which was invented in 1886.

Cellulose containing 11-12% of nitrogen is called *collodion cotton*. Its solution in a mixture of alcohol and ether is known as *collodion* and is used in medicine. Formerly cellulose nitrate was used extensively to make *celluloid*, film, and quick-drying, inexpensive, and fast nitro-lacquers and enamels. In the manufacture of celluloid, collodion cotton is mixed, while heated, with camphor and a small amount of alcohol, and the mass thus obtained is passed through heated rollers. This produces thin plates, which are then compressed in the hot state by hydraulic presses. Celluloid serves to make a variety of consumer

* The term nitration is here used loosely; in the strict sense nitration means the formation of nitrogen compounds in which the nitro group is linked to carbon: $C-NO_2$.

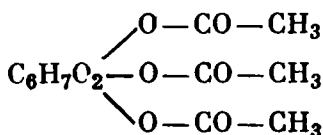
goods. In the manufacture of cinema film, collodion cotton and camphor are dissolved in a mixture of acetone and amyl alcohol; the resulting solution is poured through a thin slit onto a moving metal ribbon. The film obtained after the greater part of the solvents have been evaporated is dried with air.

At present, owing to its inflammability and the consequent fire hazard, celluloid has lost its importance and is everywhere being replaced by less flammable plastics. In the production of cinema film cellulose nitrate, because of the fire hazard, is likewise being replaced by the nonflammable cellulose triacetate.

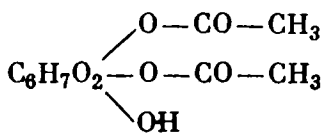
Nitro-lacquers are solutions of collodion cotton in organic solvents with special additions (diluent, plasticizers), which serve to impart to the film the required properties (adherence to the surface being painted, durability, elasticity). The addition of mineral or organic pigments to the nitro-lacquers produces nitro-dyes and enamels.

Nitro-lacquers, dyes, and enamels are used extensively for painting. Considerable amounts of them go to paint motor-cars.

The cellulose esters with acetic acid are called *cellulose acetates*:



cellulose triacetate



cellulose diacetate

Acetate rayon is made from solutions of cellulose acetate in acetone. Plasticized cellulose acetate and cellulose acetobutyrate (a mixed ester of cellulose with acetic and butyric acids) are used in the manufacture of plastics. Steering wheels for cars and other articles are made from them by injection moulding.

Apart from the cellulose esters, there are also cellulose ethers. One example of these is triethyl cellulose $\text{C}_6\text{H}_7\text{O}_2(\text{OC}_2\text{H}_5)_3$, which is formed when alkal cellulose is treated with ethyl chloride in the presence of an alkali.

It is used in the manufacture of ethyl cellulose plastics. The water-soluble cellulose ester prepared by esterification with chloroacetic acid, *carboxymethyl cellulose*, has many applications as a surface-active agent (in oil-drilling, in the production of detergents to enhance dispersancy and foaming, and in the textile industry in dyeing and finishing).

175. Rayon. The chemical processing of cellulose has acquired enormous scale owing to the exceedingly swift expansion of the artificial fibre industry, also called the rayon industry.

There are several methods of rayon production, the most important being the viscose process.

1. *Viscose Rayon*. In the production of viscose rayon the cellulose is treated with sodium hydroxide. The treatment turns it into alkal cellulose, which is then treated with carbon disulphide in big, slowly rotating drums. This produces an orange-coloured mass, which is a sodium xanthate ester of cellulose ($C_6H_9O_4O-CS-SNa)_n$ (p. 381). The xanthate is dissolved in a weak solution of sodium hydroxide

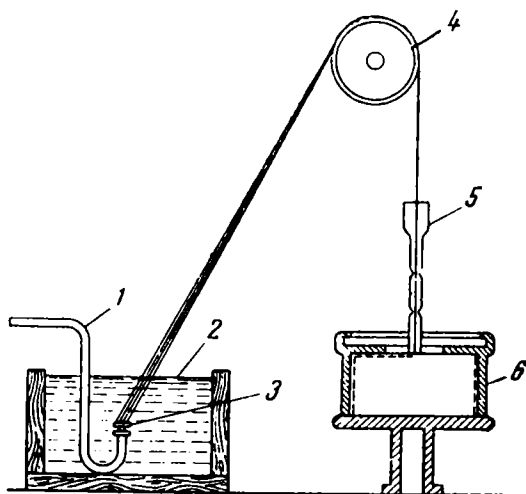


Fig. 55. Set-up for obtaining viscose rayon:

1—tube through which viscose is fed; 2—setting bath; 3—spinnerette; 4—rollers; 5—glass funnel; 6—centrifuge.

with the formation of a viscous solution called *viscose*. The treatment of viscose with acid neutralizes the sodium hydroxide and causes the xanthate to lose carbon disulphite. The resulting cellulose hydrate is recovered from the solution.

A set-up for obtaining viscose filaments is shown in Fig. 55.

The viscose, fed at a definite rate through tube 1 immersed in setting bath 2 containing a solution of sodium sulphate and sulphuric acid, is spun through a number of orifices of 0.1 mm diameter in spinnerette 3, which is attached to the end of the tube. The resulting yarn, consisting of 40-60 filaments (according to the number of orifices in the spinnerette), is first led upwards over the revolving roller 4 and then downwards through glass funnel 5 into the swiftly revolving (5,000-6,000 revolutions per minute and more) aluminium drum of centrifuge 6. Centrifugal force presses the yarn against the walls of the drum, so that it is reeled evenly into skeins.

When viscose is forced into a setting bath through narrow slits, thin transparent films of cellophane are obtained, which are plasticized with glycerol to improve their mechanical properties. Cellophane is used extensively for wrapping purposes in the food and perfumery industries.

The raw material for viscose is bisulphite wood pulp cellulose.

2. *Acetate Rayon*. This is made from cellulose acetate dissolved for this purpose in acetone. The solution is exuded from the orifices of a spinnerette and descends, in the form of a beam of threads, meeting a current of warm air, which carries off the solvent vapours. The method is known as dry spinning. The raw material for acetate rayon is cotton in the form of linters up to 5 mm long (the linters are the short stiff fibres remaining on cotton seeds after the removal of the longer fibres).

3. *Cuprammonium Rayon*. This is made from a cellulose solution in Schweitzer's reagent. The cellulose solution is forced through the orifices of the spinnerette into a bath containing warm water and weak sulphuric acid. In this bath the cellulose is precipitated from the solution, forming threads. Cotton linters are the raw material for cuprammonium rayon.

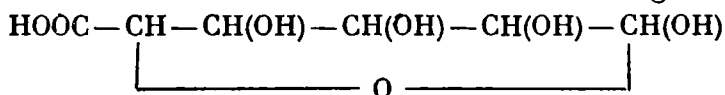
Artificial fibre production dates back to 1884, when the first artificial fibre mill was built in France.

Russia before the revolution had practically no artificial fibre production. There was only one mill (near Moscow), which manufactured about 100 tons of artificial fibre a year. In the past 30 years a huge rayon industry has been built up in the U.S.S.R.

176. *Hemicelluloses and Pectins*. The walls of plant cells, in addition to cellulose, always contain carbohydrates very similar to cellulose, which are called *hemicelluloses*. These are divided into hexosans ($C_6H_{10}O_5$)_x and pentosans ($C_5H_8O_4$)_x. The hexosans, upon hydrolysis, yield glucose and other hexoses (galactose, fructose); the hydrolysis products of the pentosans are xylose and arabinose. The hemicelluloses undergo hydrolysis more readily than cellulose does; unlike cellulose, they dissolve in alkalis.

Closely related to the pentosans are the *gums* and *pectin substances*, or vegetable secretions. The gums are plant juices that have solidified in the air, such as cherry-tree gum and gum arabic, the solidified juice of the tropical acacia.

Large quantities of pectin substances are contained in the fruits of certain plants: gooseberries, strawberries, and apples. Thanks to their presence, fruit syrups with sugar heated to boiling point and then cooled will form jellies. This property of pectins is used in making candied fruit jellies, jelly, and certain other sweets. Pectins are calcium and magnesium salts of *polygalacturonic acid*. D-galacturonic acid is one of the stereoisomeric acids of the general formula:



It can be regarded as an oxidation product of the CH_2OH group in D-galactose. The D-galacturonic acid residues in poly-D-galac-

turonic acid are linked in the same manner in which the glucose residues are linked in a cellulose molecule.

Part of the carboxyl groups in the pectins are esterified by methyl groups. Natural pectins are mixed with polysaccharides, which upon hydrolysis yield D-galactose (galactans) and D-arabinose (arabans).

Lignin. Lignin is one of the principal substances embedded in cellulose. The wood of the pine contains 34% of lignin, the wood of the beech, 22.5%. Lignin contains carbon, hydrogen, and oxygen, the percentage of carbon being higher than in cellulose. The exact composition of lignin has not been determined. It is less resistant to chemical action than cellulose is. The presence of considerable numbers of methoxy groups in the lignin molecule accounts for the formation of methyl alcohol in the dry distillation of wood.

Methyl alcohol is not formed, however, in the dry distillation of pure cellulose. The fusing of lignin with an alkali or its oxidation by ozone yields compounds of the aromatic series.

Nitrogen Compounds

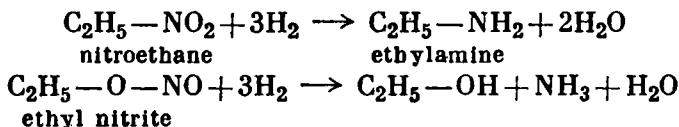
177. Structure of Nitrogen Compounds and Their Preparation.

The nitrogen compounds are substances containing the NO_2 nitro group, the nitrogen atom being linked directly to a carbon atom.

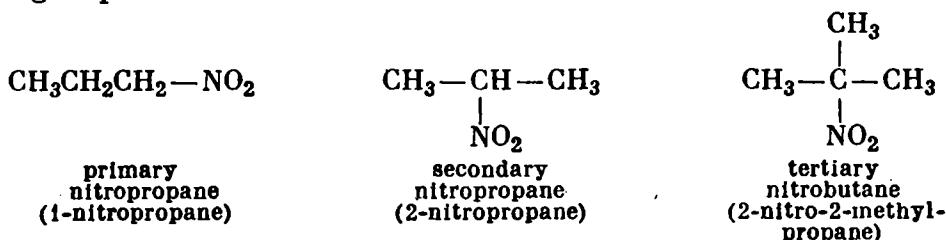
Nitromethane $\text{CH}_3\text{—NO}_2$ and nitroethane $\text{C}_2\text{H}_5\text{—NO}_2$ are examples of nitrogen compounds. They are isomers of nitrous acid esters, but have higher boiling points.

Nitro compounds	B.p., °C	Nitrous acid esters	B.p., °C
$\text{CH}_3\text{—NO}_2$	101.5	$\text{CH}_3\text{—O—NO}$	−12
$\text{CH}_3\text{—CH}_2\text{—NO}_2$	114.0	$\text{C}_2\text{H}_5\text{—O—NO}$	17
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—NO}_2$	131.6	$\text{C}_3\text{H}_7\text{—O—NO}$	57

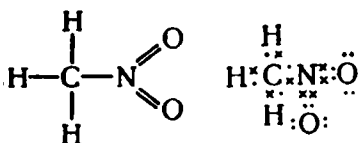
Reduction turns the nitro compounds into amines, whereas the esters are converted into alcohols and ammonia:



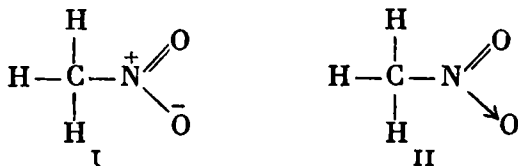
There are three classes of nitro compounds—primary, secondary, and tertiary—according to the carbon atom to which the nitro group is attached:



If we assume that the nitrogen atom in the nitro compound molecule is doubly bound with each of the oxygen atoms, the electronic formula of the compound will be at variance with the octet rule, since the nitrogen atom will be surrounded by ten electrons:



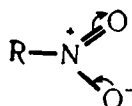
As this is impossible, we have to accept a different electron arrangement usually represented by formula I or formula II:



These formulas imply that the oxygen atoms attached to the nitrogen are, as it were, not equivalent: one is linked to the nitrogen atom by two pairs of common electrons, while the other is linked by only two electrons, with both electrons being furnished by a single atom, the nitrogen atom; these electrons bring the number of the oxygen atom's electrons up to an octet. The oxygen atom in this case acquires a negative charge, while the nitrogen atom acquires a positive charge, since the electron pair no longer belongs to it alone. Such bonds are called *semipolar*. Substances with semipolar bonds have high dipole moments and usually boil at higher temperatures than isomeric substances without semipolar bonds.

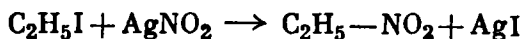
The above structural formulas of nitro compounds are simplified; in reality, as recent investigations have shown, both oxygen atoms in these compounds are absolutely equivalent.

It is customary to use curved arrows in such cases to show the direction of the electron density shift:



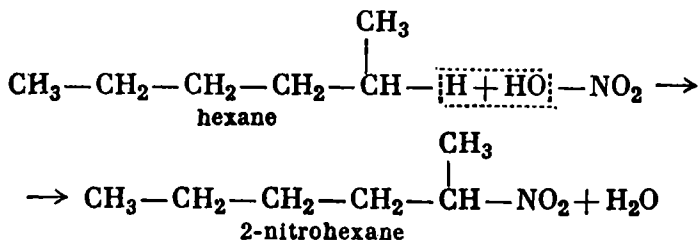
The nitrogen derivatives of the saturated hydrocarbons are called *nitroparaffins*.

Nitroparaffins were first prepared by the action of silver nitrite on alkyl halides:



A certain amount of nitrous acid esters is produced simultaneously with the nitro compounds.

M. Konovalov (1886) found that nitroparaffins can be prepared by heating saturated hydrocarbons with dilute HNO_3 to $130\text{--}140^\circ$ in sealed tubes:



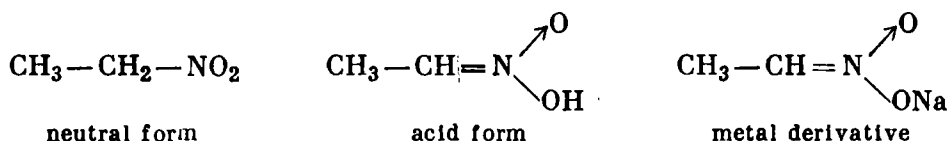
Substitution takes place at a lesser hydrogenated carbon atom.

The Konovalov reaction has lately been used industrially for the nitration of petroleum hydrocarbons.

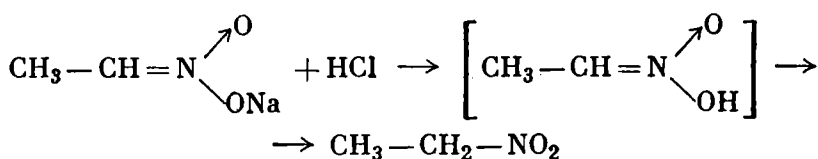
Nitration is usually conducted by subjecting the hydrocarbons in the vapour phase to the action of nitrogen dioxide.

178. Properties of Nitrogen Compounds. The lower homologues of the nitroparaffin series are colourless liquids with a pleasant odour, which are miscible with alcohol and with ether. They do not conduct electricity, have a low solubility in water, and are neutral substances. Primary and secondary nitro compounds do, however, dissolve slowly in solutions of caustic alkalis, causing their neutralization.

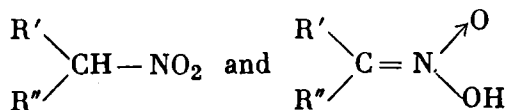
In primary and secondary nitro compound molecules the hydrogen atom linked to the same carbon atom that is connected with the nitro group can be replaced by a metal. If, for example, alcoholic solutions of nitroethane $C_2H_5NO_2$ and sodium ethylate are mixed, crystalline $C_2H_4NaNO_2$ is precipitated. These metal derivatives are readily soluble in water. In aqueous solution they are, judging by the electric conductivity, highly ionized; their litmus reaction is neutral, i.e., they are salts of strong acids. They should be regarded as salts of acids tautomeric to neutral nitro compounds:



The acid forms of nitrogen compounds are often called *isonitrocompounds**. The addition of an acid to a metal derivative produces the acid form, which is then isomerized to a neutral nitro compound:

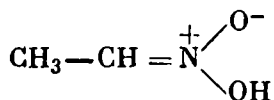


Secondary nitro compounds behave in quite the same way. They too can react in two tautomeric modifications:



The nitro group thus imparts a mobility to the hydrogen atom attached to the same carbon atom. In tertiary nitro compounds the

* The structure of isonitrocompounds can also be represented thus:

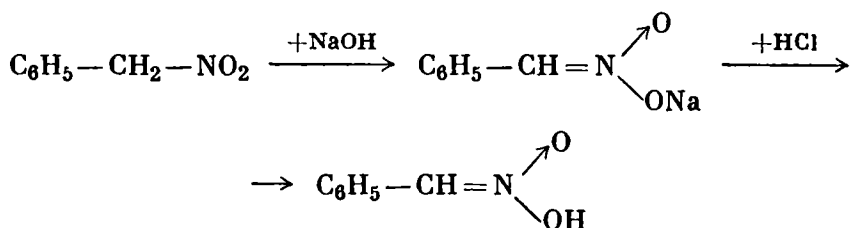


carbon atom with the nitro group has no hydrogen atom, and the hydrogen in such nitro compounds cannot be replaced by a metal.

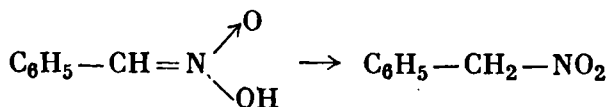
It has not been possible to isolate the acid forms of nitrogen compounds of the paraffin series, but this has been possible in the case of saturated aromatic compounds.

In 1896 Konovalov and co-workers demonstrated that phenylnitromethane can exist in two modifications.

Phenylnitromethane $\text{C}_6\text{H}_5\text{—CH}_2\text{—NO}_2$ can be viewed as nitromethane $\text{CH}_3\text{—NO}_2$ in whose molecule one hydrogen atom has been replaced by phenyl. It is an oily liquid boiling at $225\text{--}227^\circ$. When phenylnitromethane is dissolved in an alkali and the resulting solution acidified, a crystalline substance is precipitated which melts at 84° and has the composition of phenylnitromethane:



Within a few hours it changes into liquid phenylnitromethane:



The acid form of phenylnitromethane is readily soluble in water; the solution at first exhibits a high electric conductivity, which gradually, with the isomerization of the phenylnitromethane to the neutral form, diminishes and at last ceases to be at all appreciable.

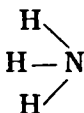
Neutral substances which under the action of alkalis yield salts of isomeric strong acids are called *pseudo-acids*.

Amines

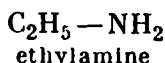
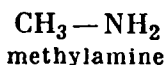
179. Structure of Amines. *The amines are derivatives of ammonia, in which one or several hydrogen atoms have been replaced by hydrocarbon radicals.*

Primary, secondary, and tertiary amines are distinguished according to the number of hydrogen atoms replaced by hydrocarbon radicals.

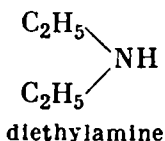
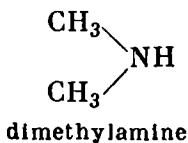
Ammonia:



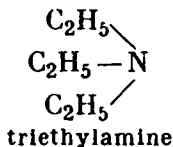
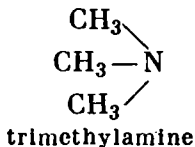
Primary amines:



Secondary amines:



Tertiary amines:



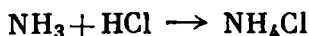
The $-\text{NH}_2$ group in primary amines is called the *amino group*. The $>\text{NH}$ group in secondary amines is called the *imino group*.

180. Properties of Amines. Methylamine, dimethylamine, and trimethylamine are gases; the intermediate members of the amine series are liquids, and the higher members are solids. With the increase in molecular weight there is a rise in relative density and boiling point, but a drop in water solubility, the higher amines being insoluble in water. The lower amines have odours somewhat resem-

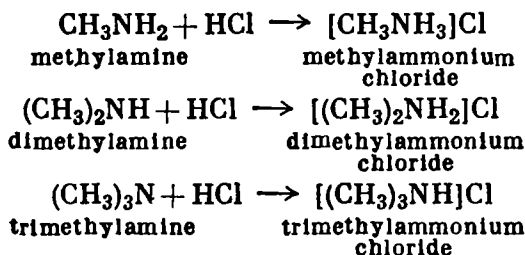
bling the odour of ammonia. The higher amines are either odourless or have a very faint odour.

In chemical properties the amines are very similar to ammonia.

1. A characteristic property of ammonia is, of course, its ability to combine with acids, forming ammonium salts:



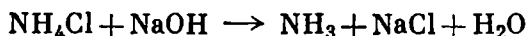
The amines combine with acids in the same way to form salts similar to ammonium salts:



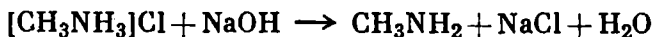
These compounds can be regarded as derivatives of ammonium salts, in which one or several hydrogen atoms have been replaced by hydrocarbon radicals.

The formulas of the amine salts are usually written not in the form used above, but with a dot to separate the formula of the amine from the formula of the acid. For instance, methylammonium chloride $(\text{CH}_3\text{NH}_3)\text{Cl}$ is looked upon as $\text{CH}_3\text{NH}_2 \cdot \text{HCl}$ and is called methylamine hydrochloride, just as ammonium chloride NH_4Cl used to be viewed as ammonia hydrochloride $\text{NH}_3 \cdot \text{HCl}$.

2. Alkalis easily decompose ammonium salts with the evolution of free ammonia:

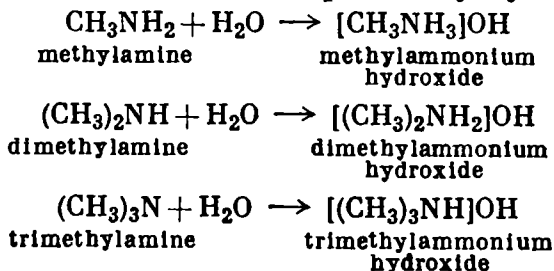


Amine salts are similarly decomposed by alkalis with the formation of a free amine:



3. An aqueous solution of ammonia turns litmus blue, i.e., has alkaline properties; aqueous solutions of fatty amines likewise turn litmus blue.

The alkaline properties of amine aqueous solutions are due to the presence of derivatives of ammonium hydroxide, in which one or several hydrogen atoms have been replaced by hydrocarbon radicals:



These hydroxides have more pronounced basic properties than ammonium hydroxide.

A comparison of the properties of ammonia and the amines thus shows that the amines, as derivatives of ammonia, have many of its properties. In other words, the amines are organic bases.

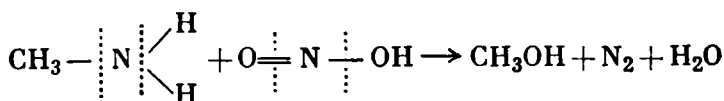
In most cases organic bases with fatty radicals are stronger bases than ammonia, i.e., they are more highly ionized in aqueous solutions and have a higher basicity. The ionization constants of ammonia and some organic bases are given in Table 12.

TABLE 12. Ionization Constants of Ammonia and Some Organic Bases

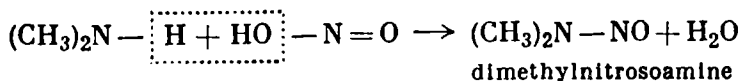
Base	Ionization constant	Base	Ionization constant
Ammonia	1.79×10^{-5}	Dimethylamine . .	5.20×10^{-4}
Methylamine	4.38×10^{-4}	Trimethylamine . .	5.45×10^{-4}
Ethylamine	5.60×10^{-4}	Diethylamine . . .	9.6×10^{-4}
<i>n</i> -Propylamine . . .	4.70×10^{-4}	Triethylamine . . .	6.4×10^{-4}
Isopropylamine . . .	5.30×10^{-4}	Dipropylamine . .	1.02×10^{-3}
<i>n</i> -Butylamine	4.1×10^{-4}	Tripropylamine . .	5.5×10^{-4}
Isobutylamine	3.1×10^{-4}	Diisobutylamine . .	4.8×10^{-4}
Isoamylamine	5.0×10^{-4}		

Unlike ammonia, the amines can burn in the air. It was, in fact, this combustibility of the amines that led to their discovery (1848). Wurtz at first mistook the vapours of ethylamine (b.p. 17°) for ammonia, but then he happened to notice that this gas with the odour of ammonia can burn in the air.

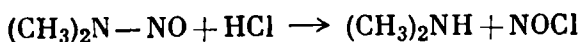
Action of Nitrous Acid on Amines. The action of nitrous acid on primary amines causes free nitrogen to be evolved and alcohols to be formed:



Secondary amines react with nitrous acid to form *nitrosoamines*, yellowish liquids with a low solubility in water:

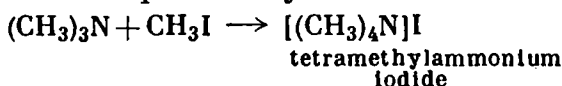


The treatment of nitrosoamines with concentrated hydrochloric acid reconverts them into the initial amines:



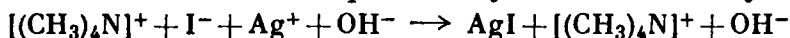
Tertiary amines are stable to the action of nitrous acid (they form salts of nitrous acid).

Quaternary Ammonium Salts. The heating of tertiary amines with alkyl halides produces quaternary ammonium salts:



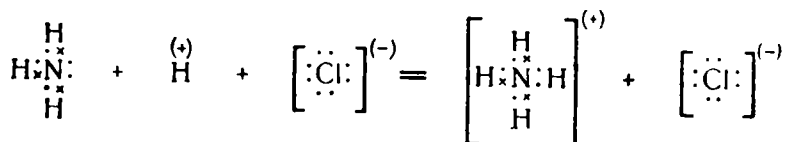
These compounds are crystalline substances, which are soluble in water and dissociate readily in aqueous solution.

The action of silver hydroxide upon quaternary ammonium iodides produces solutions of quaternary ammonium hydroxides:

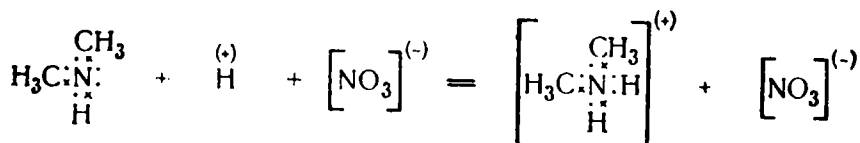


These hydroxides are alkalis as strong as sodium hydroxide or potassium hydroxide. Tetramethylammonium hydroxide $[(\text{CH}_3)_4\text{N}]\text{OH}$ can be prepared in the form of a white solid substance with a marked resemblance to the caustic alkalis.

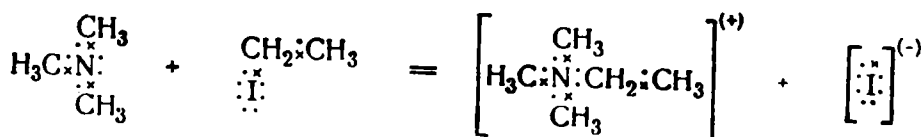
181. Structure of Ammonium Salts. The formation of ammonium chloride from ammonia and hydrochloric acid can be depicted as follows. In the ammonia molecule three of the five valency electrons of the nitrogen go to form the covalent linkages with the three hydrogen atoms. The nitrogen atom is thus left with a free electron pair. The hydrogen ion (proton) of the acid links up with this free electron pair of the nitrogen, forming an ammonium ion with a positive charge:



Once the ammonium ion is formed it is obviously no longer possible to identify the hydrogen atom that "made use" of the available electron pair of the nitrogen. It is equally obvious that the chlorine ion is no longer related to any particular hydrogen atom. The structure of the amine salts can be depicted similarly:



Alkyl halides combine with tertiary amines in the same way:

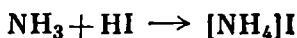


The amine salts should be regarded as complex compounds; the nitrogen atom serves as the central atom, its co-ordination number being four. The hydrogen atoms and the alkyls are linked to the nitrogen atom and are in the inner co-ordination sphere, whereas the acid radical or hydroxyl is in the outer co-ordination sphere and is detached as an ion in electrolytic dissociation.

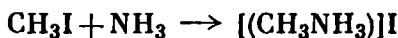
182. Preparation of Amines. Amines can be prepared by various methods.

1. Action of Ammonia on Alkyl Halides (Hofmann's Reaction). In bringing about this reaction an alcoholic solution of ammonia is heated with an alkyl halide. As a specific instance of this reaction let us consider the action of ammonia on methyl iodide.

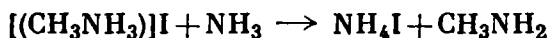
Ammonia adds a molecule of hydrogen iodide to form ammonium iodide:



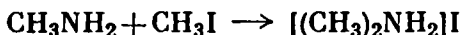
Similarly, the action of ammonia on methyl iodide produces methylammonium iodide:



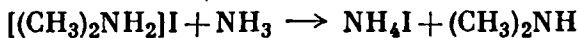
Part of the methylammonium iodide produced is decomposed by excess ammonia with the formation of free methylamine



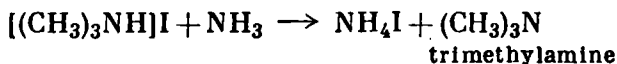
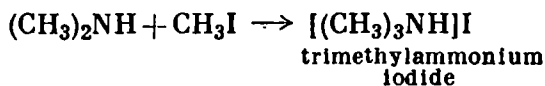
which again combines with methyl iodide, yielding dimethylammonium iodide:



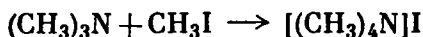
The latter is decomposed by ammonia with the formation of free dimethylamine:



Trimethylamine is subsequently also formed:



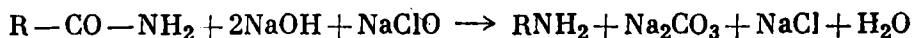
Finally, a molecule of trimethylamine adds another molecule of methyl iodide, forming tetramethylammonium iodide



which is a quaternary ammonium salt. The reactions thus produce a mixture of substituted ammonium salts.

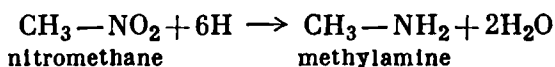
2. Heating of Acid Amides with Alkaline Solutions of Hypobromites and Hypochlorites. This reaction involves a rearrangement where-

by the amino group becomes directly linked to the radical. The mechanism of the reaction is highly complicated; the ultimate result can be expressed by the equation:



The reaction was discovered by Hofmann* in 1881. It is of industrial importance, being used, for instance, to manufacture anthranilic acid (p. 548), a semi-product in the synthesis of indigo.

3. *Reduction of Nitrogen Compounds.* This can be brought about, for example, by tin and hydrochloric acid:



The preparation of amines from nitrogen compounds was until recently of little importance, since nitrogen compounds were not readily available. But advances in the nitration of paraffins resulting from the work of A. Topchiyev and A. Titov make this method highly promising.

The preparation of amines from nitriles and isocyanates is discussed elsewhere (pp. 367 and 372).

Amines are formed naturally by the decay of organic remains containing protein substances.

183. Some Representative Amines. *Methylamine* CH_3NH_2 is formed in the dry distillation of bones. In the free state it is a gas, which condenses into a liquid at -6.3° . It has an odour like that of ammonia and also resembling the smell of fish. Methylamine dissolves very readily in water.

Dimethylamine $(\text{CH}_3)_2\text{NH}$ is contained in the brine in which herrings have been cured and is formed in the decay of fish. It condenses into a liquid at 6.9° .

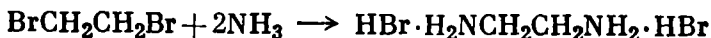
Trimethylamine $(\text{CH}_3)_3\text{N}$ is contained in herring brine and in certain plants; it is formed in the dry distillation of beet molasses and condenses into a liquid at 2.8° .

Ethylenediamine $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (1,2-diaminoethane) is the simplest of the diamines, i.e., amines with two amino groups in the molecule. The diamines dissolve readily in water, have a characteristic odour, react strongly alkaline, and interact with the carbon dioxide of the air. They form stable salts with two acid equivalents.

* August Wilhelm von Hofmann (1818-92) worked for a long time in London and then, from 1864, in Berlin. Hofmann accomplished the synthesis of primary, secondary, and tertiary fatty amines by the action of ammonia on halogen derivatives. He carried out a study of these amines, as well as research in the chemistry of the aromatic amines.

Hofmann also discovered benzene in coal-tar and turned it into nitrobenzene; he studied the dye indigo and synthesized two other important dyes: fuchsin and rosaniline.

Ethylenediamine can be prepared by the action of ammonia upon ethylene dibromide:



Ethylenediamine is a liquid with an ammoniacal odour. Its b.p. is 116.5° ; its m.p., 8.5° .

Tetramethylenediamine (1,4-diaminobutane), or *putrescine*



and *pentamethylenediamine* (1,5-diaminopentane), or *cadaverine*



were discovered in the products of the decomposition of proteins and are known as *ptomaines* (from the Greek *ptoma* meaning corpse); they used to be referred to as "ptomaine poisons". It has now been established that the poisonous nature of decaying proteins is due to the presence not of ptomaines, but of certain other substances of unknown chemical nature.

Putrescine and cadaverine are formed as a result of the activity of many bacilli (such as the pathogenes of tetanus and cholera) and moulds; they occur in cheese, ergot, the fly mushroom, and brewing yeast.

Putrescine was first found in puss. It is a crystalline substance (m.p. $27-28^\circ$; b.p. $158-160^\circ$). *Cadaverine* is a liquid boiling at $178-179^\circ$; it was found in decomposing cadavers. The reactions establishing the structure of these diamines will be found on p. 347. Both putrescine and cadaverine are strong bases.

Spermine $\text{NH}_2[\text{CH}_2]_3\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}[\text{CH}_2]_3\text{NH}_2$ is a tetramine. It may be regarded as putrescine in whose molecule two hydrogen atoms—one in each amino group—have been replaced by two aminopropyl groups, their NH_2 groups being attached to γ -carbon atom. Spermine is di-N,N'-(γ -amino-propyl)-putrescine. It has been isolated from the human sperm. Its most readily available source is the pancreas of cattle. Spermine is a crystalline substance and reacts strongly alkaline.

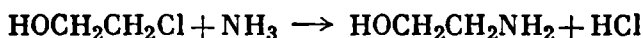
Some diamines have lately found extensive application as raw materials in the production of polyamide fibres and plastics. Nylon, for instance, is produced from hexamethylenediamine $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (p. 363).

Aminoalcohols and Amino Acids

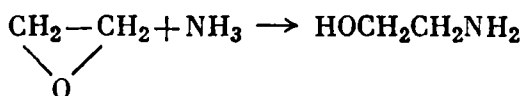
184. Aminoalcohols. Aminoalcohols are compounds with mixed functions, whose molecules contain amino and hydroxy groups. A well studied aminoalcohol of great interest is ethanolamine, or *colamine*, $\text{HO}-\text{CH}_2\text{CH}_2-\text{NH}_2$.

The structure of ethanolamine (2-aminoethanol-1) becomes clear from the reactions of its preparation.

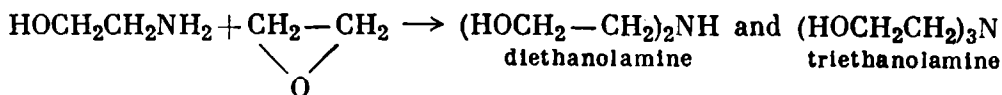
1. Ethanolamine can be prepared by the action of ammonia on ethylene chlorohydrine:



2. Ethanolamine can be prepared by the addition of ammonia to ethylene oxide:

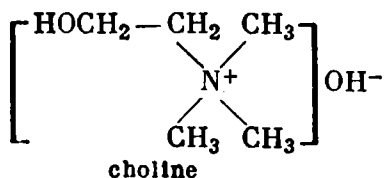


Ethanolamine is a thick oil (b.p. 171°) miscible with water in all proportions; it has pronounced alkaline properties. The above methods of preparation yield monoethanolamine together with diethanolamine and triethanolamine:



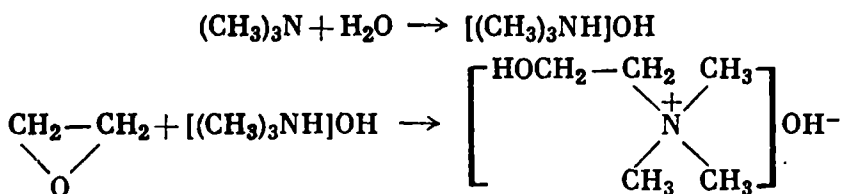
The ethanolamines have many industrial uses as emulsifying agents and detergents, and also for removing carbon dioxide from furnace gases in the production of liquid carbon dioxide and dry ice.

Choline is a quaternary ammonium hydroxide. In it the nitrogen atom is linked with three methyl and one hydroxyethyl group:



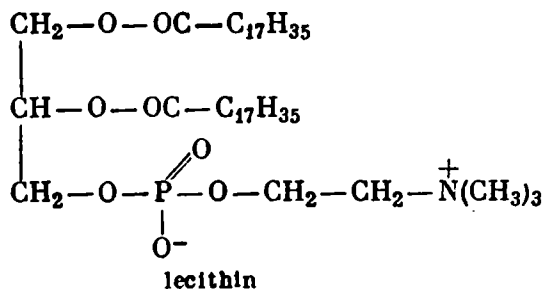
Choline is hydroxyethyltrimethylammonium hydroxide.

It is a constituent of lecithins, which are fat-like substances; it is highly widespread in animal and plant organisms and can be isolated from them. Synthetic choline is prepared by treating a concentrated solution of trimethylamine with ethylene oxide at ordinary temperature:

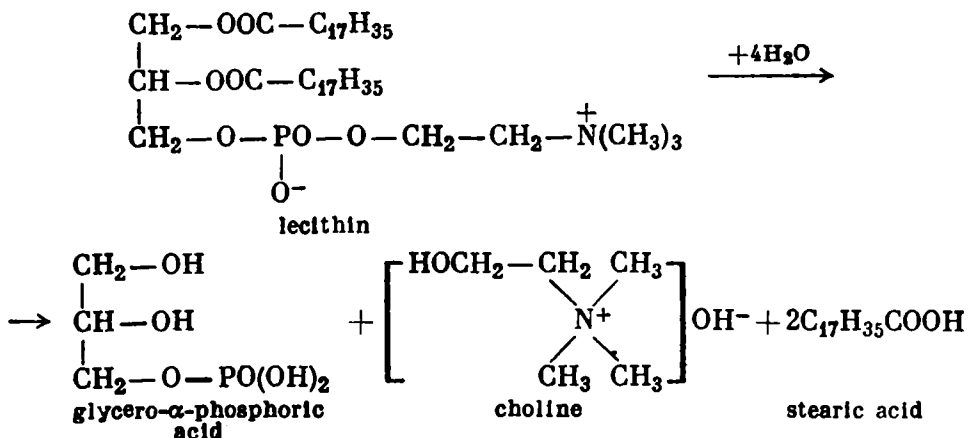


Choline is a crystalline, highly hygroscopic and deliquescent mass. It has pronounced alkaline properties and readily forms salts with acids.

Lecithins are esters of glycerol in whose molecules two hydroxyls have been esterified by fatty acids, while the third has been esterified by phosphoric acid, which in turn has formed an ester with choline, e.g.*:

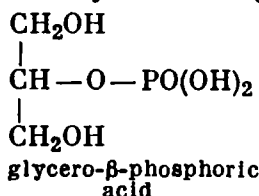


Upon heating with dilute acids or alkalis, lecithins are hydrolyzed and form choline, fatty acids, and optically active glycerol- α -phosphoric acid:



* This formula implies an intramolecular (betaine) bond between phosphoric acid and the choline residue (p. 345).

Less widespread are lecithins in whose molecules the β -hydroxyl of glycerol has been esterified by phosphoric acid. The hydrolysis of these lecithins produces optically inactive glycerol- β -phosphoric acid:



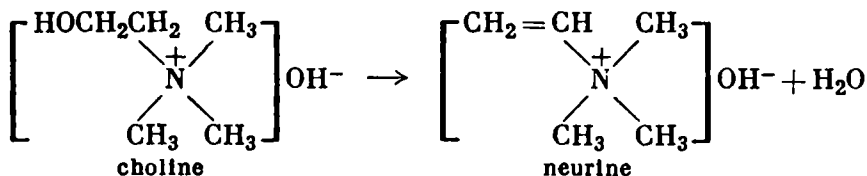
Lecithins occur in nearly all animal and plant organisms.

Especially rich in lecithins are the brain, nerve tissues, sperm, and egg yolk (9.4%) (the Greek *lekithos* means yolk); in plants lecithins are particularly abundant in seeds and sprouts. Many lecithins have been prepared synthetically.

Lecithins are poorly crystallizing substances. In water they usually swell and form colloid solutions.

They have a very high adsorption capacity with respect to most diverse substances: proteins, sugars, alkaloids, etc.

The putrefaction of lecithins or the boiling of choline with baryta water causes the hydroxyethyl group of choline to lose water with the formation of vinyltrimethylammonium hydroxide, or *neurine*:

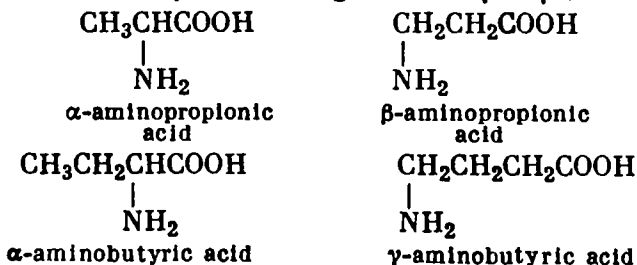


Neurine is a syrupy mass with highly alkaline properties; it is very poisonous.

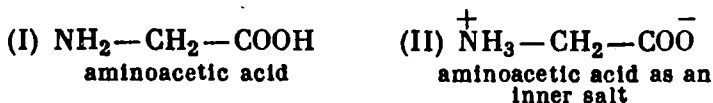
Cephalins, unlike lecithins, contain a colamine residue instead of the choline residue (p. 338); they are contained in brain matter and can be isolated from it.

185. Structure of Amino Acids and Their Preparation. *Amino acids are compounds whose molecules contain both an amino and a carboxyl group.* They are therefore both bases and acids at the same time, for example aminoacetic acid $\text{NH}_2\text{—CH}_2\text{—COOH}$.

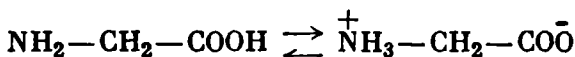
According to the position of the amino group with respect to the carboxyl, it is customary to distinguish α -, β -, γ -, etc., amino acids:



The amino acids are at present viewed as products of the mutual neutralization of the carboxyl and the amino group in one and the same molecule, i.e., as inner salts:

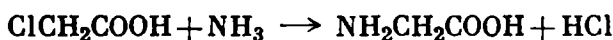


An inner salt molecule is an ion with different charges at its opposite ends, a dipolar ion. It is an ionized molecule, but cannot undergo dissociation. In a solution part of the molecule are in the state depicted by formula I, i.e., there is an equilibrium:

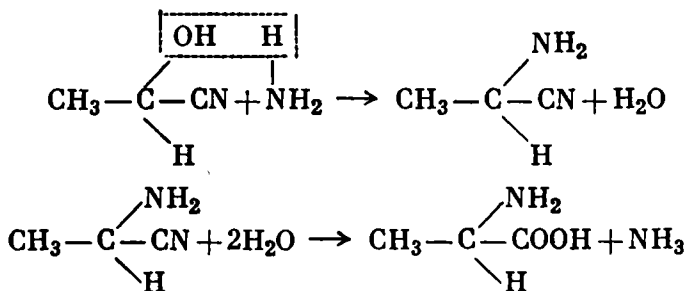


The amino acids are very important physiologically: they are formed by the hydrolysis of protein substances in animal and plant organisms.

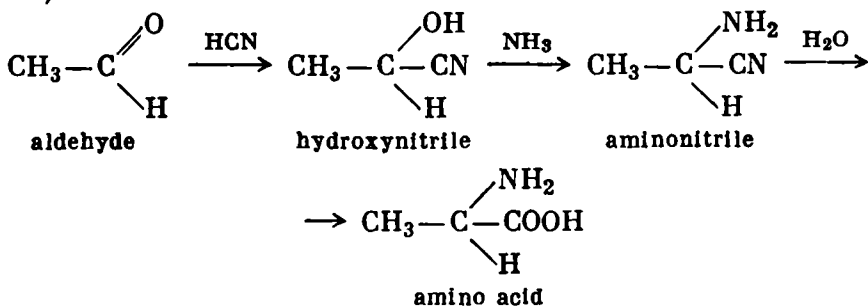
Just as amines are formed by the action of ammonia upon halogen derivatives of hydrocarbons, amino acids may be prepared by the action of ammonia upon halogenated acids:



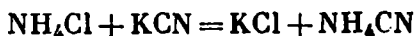
Alpha-amino acids are prepared by the action of ammonia upon hydroxynitriles; this at first produces amino nitriles, which upon saponification yield corresponding amino acids:



Since hydroxynitriles are formed by the addition of hydrogen cyanide to aldehydes and ketones, the reaction makes it possible to convert aldehydes and ketones into amino acids (cyanohydrin synthesis):

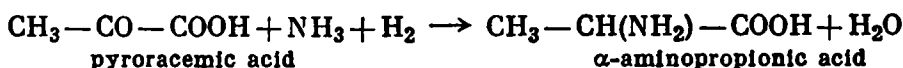


As shown by N. Zelinsky and his pupils, it is simplest to prepare α -amino acids by the action of aqueous solutions of potassium cyanide and ammonium chloride upon aldehydes and ketones. An exchange reaction produces potassium chloride and ammonium cyanide:



The ammonium cyanide reacts with the aldehyde or ketone to form an amino nitrile.

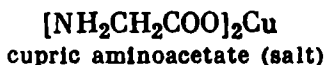
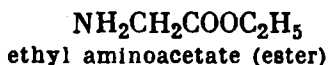
Amino acids are likewise formed by the catalytic reduction of keto acids by hydrogen in the presence of ammonia or amines:



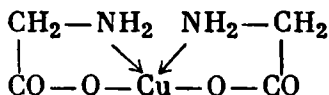
It should be mentioned that the catalyst and hydrogen can be replaced by cysteine (p. 347), i.e., a normal constituent of proteins. This is possibly the way in which amino acids are formed in nature.

Properties of Amino Acids. 1. Most of the amino acids are colourless crystalline substances, which are usually readily soluble in water and often have a sweetish taste.

2. The amino acid molecules contain two groups with directly opposite properties: the carboxyl group with acidic properties and the amino group with basic properties. For this reason they possess both acidic and basic properties at the same time. As acids the amino acids form esters with alcohols, while with metals and bases they form salts:



Especially characteristic of the amino acids is the formation of copper salts with a specifically blue colour. These are inner complex salts in which the copper atom is linked not only to the oxygen atoms, but also to the nitrogen atoms of the amino groups:



The linkage between the copper and nitrogen atoms is effected by *additional* valencies (at the expense of the free electron pair of the amino group nitrogen). It will be remembered that nickel dimethylglyoximate and metal acetylacetae are also chelate compounds (p. 204).

The action of caustic alkalis upon copper salts of the amino acids does not precipitate cupric hydroxide. Hydrogen sulphide, however, breaks up the inner complex, precipitating cupric sulphide, which has a very low solubility in water.

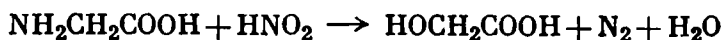
The acidic properties of the monoamine acids are not very pronounced: they scarcely alter the colour of litmus. The acidic properties of the carboxyl in them have thus been greatly attenuated

As amines the amino acids react with acids to form salts such as:



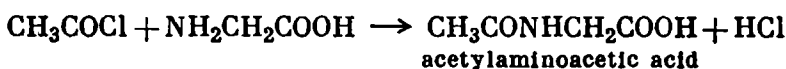
But these salts are highly unstable and decompose readily. The basic properties of the amino group in the amino acids are thus likewise much weakened.

3. Amino acids react with nitrous acid to form hydroxy acids:



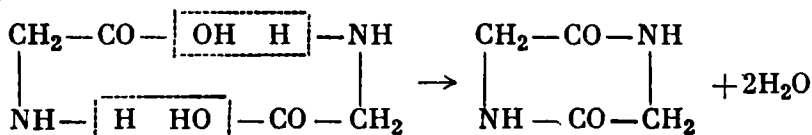
The reaction is quite similar to the formation of alcohols when primary amines are treated with nitrous acid.

4. With acid halides the amino acids form substances that are both amino acids and acid amides simultaneously. For instance, the action of acetyl chloride upon aminoacetic acid produces acetylaminopropionic acid:



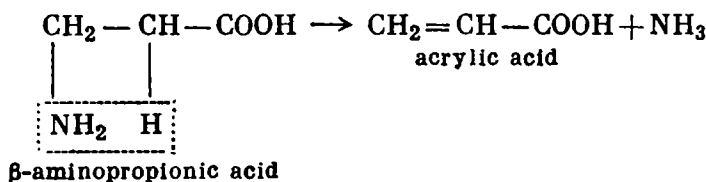
Acetylaminopropionic acid can be regarded both as a derivative of aminoacetic acid, in whose molecule a hydrogen atom of the amino group has been replaced by a CH_3CO — acetyl group, and as acetamide in whose molecule a hydrogen atom of the amino group has been replaced by the acetic acid radical $-\text{CH}_2\text{COOH}$.

5. The α -amino acids, upon heating, readily lose water; two molecules of the acid in this case lose two molecules of water, forming a *diketopiperazine*:

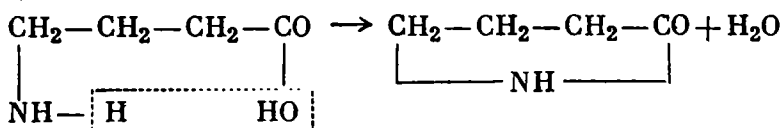


Diketopiperazines are cyclic compounds with a ring formed by four carbon atoms and two nitrogen atoms. They are solids which crystallize readily.

The β -amino acids, upon heating, lose ammonia, forming unsaturated acids:

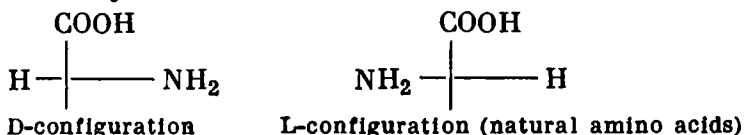


The γ -amino acids lose water readily, forming *lactams*:



Lactams may be regarded as inner amides.

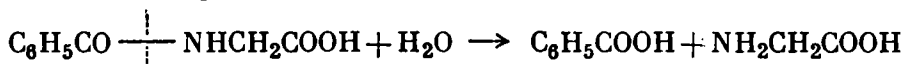
6. The molecules of most α -amino acids contain an asymmetric carbon atom; natural amino acids exist in the form of optical antipodes. The antipodes whose configuration is similar to that of dextrorotatory glyceraldehyde are designated by the letter D; the letter L denotes the antipodes whose configuration is similar to that of laevorotatory glyceraldehyde:



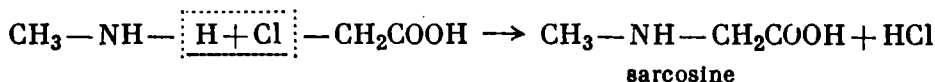
The antipodes with the amino group in 2ρ -position are referred to the D-series, while the antipodes with the amino group in 2σ -position are referred to the L-series. The α -amino acid families are thus related in configuration to the α -hydroxy acid families. The stereochemical designation of the amino acid is discussed in greater detail in Sec. 187.

186. **Some Representative Amino Acids.** *Aminoacetic acid* $\text{NH}_2\text{CH}_2\text{COOH}$, also called *glycocoll* (derived from the Greek *glukus* meaning sweet and *kolla* meaning glue) and *glycine*, occurs in the muscles of the lower animals. Large quantities of it (36% of the weight of the initial material) are formed when the protein matter of silk undergoes hydrolysis. It is prepared by boiling glue with dilute sulphuric acid or baryta water, or by subjecting hippuric acid to hydrolysis.

Hippuric acid $\text{C}_6\text{H}_5\text{CONHCH}_2\text{COOH}$ is contained in large quantities in the urine of horses. When boiled with dilute acids it forms benzoic acid and glycocoll:

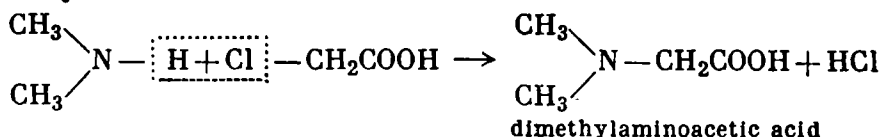


Glycocoll can be prepared synthetically from ammonia and chloroacetic acid. If the synthesis is conducted with an amine instead of ammonia, it yields glycocoll derivatives in which the hydrogen atoms attached to the nitrogen are replaced by alkyls. For example, the action of methylamine upon chloroacetic acid yields methylglycocoll, or *sarcosine*:

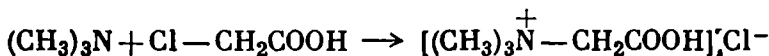


Sarcosine is formed by the hydrolysis of creatine (p. 380), a substance contained in the muscles.

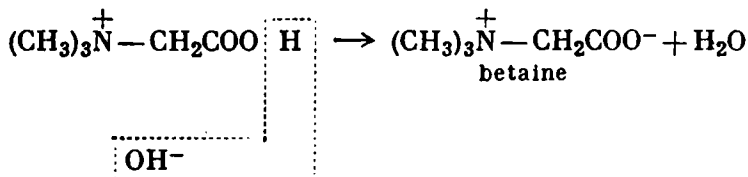
When chloroacetic acid is treated with dimethylamine the result is dimethylaminoacetic acid:



Finally, when chloroacetic acid is treated with trimethylamine, a quaternary ammonium salt is formed:



This substance is somewhat inaccurately called betaine hydrochloride. The corresponding base is unstable and, upon losing water, yields *betaine*, which should be regarded as an internal salt of a quaternary ammonium base:

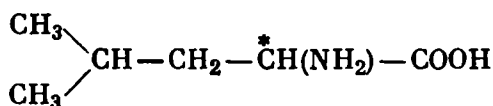


Betaine occurs in many plants. It is present, for example, in the juice of the sugar-beet (*beta* is the Latin for beet); in sugar refining it accumulates in molasses. Betaine crystallizes as a monohydrate. In water it dissolves very readily, and the aqueous solution is neutral. Anhydrous betaine melts at 293°.

Other internal salts of quaternary ammonium bases are now also called betaines.

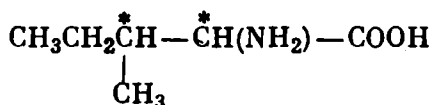
Alpha-alanine $\text{CH}_3-\overset{*}{\text{CH}}(\text{NH}_2)-\text{COOH}$ is α -aminopropionic acid (2-aminopropanoic acid). L(+)-alanine is obtained in quantity by the hydrolysis of silk fibroin; small quantities of it are formed in the hydrolysis of many protein substances.

Leucine



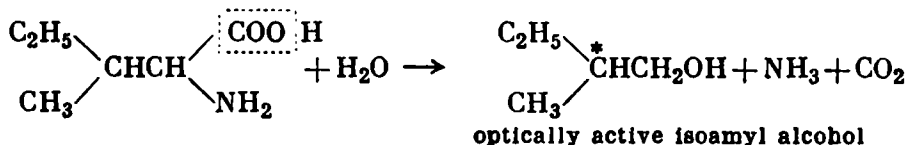
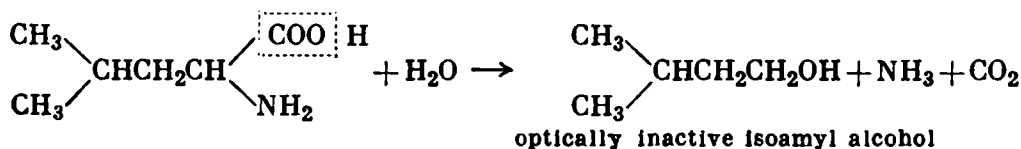
is α -aminoisocaproic acid (4-amino-2-methylpentanoic-5-acid). Considerable quantities of leucine are contained in the products of the hydrolysis of most proteins, such as the haemoglobin of the blood, casein, and egg albumin. Natural leucine forms glistening scaly crystals (the Greek word *leukos* means white). Its solution is dextrorotatory.

Isoleucine

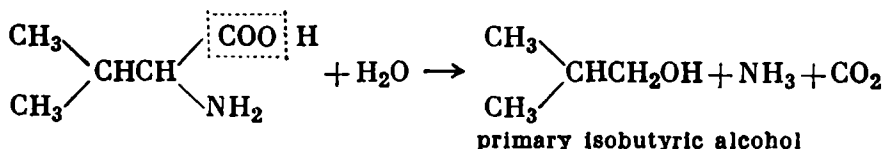


is α -amino- β -methylvaleric acid (2-amino-3-methylpentanoic acid). Small amounts of isoleucine are contained in the products of the hydrolysis of many proteins; with leucine it is contained in beet molasses. The isoleucine molecule contains two asymmetric carbon atoms; natural isoleucine is dextrorotatory.

Under the influence of certain microorganisms such as yeast, leucine and isoleucine are converted into alcohols whose molecules contain one carbon atom less than the molecules of the initial amino acids. The amino acid molecules in this case lose CO_2 , while the amino group is replaced by a hydroxyl. Leucine in this way yields optically inactive primary isoamyl alcohol, while isoleucine yields optically active primary isoamyl alcohol:



Valine (α -aminoisovaleric acid) upon fermentation yields primary isobutyric alcohol:

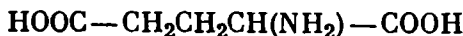


These reactions account for the formation of fusel oil alcohols in wine-making. They are formed not from sugars, but from amino acids, which arise from the proteins in the material undergoing fermentation.

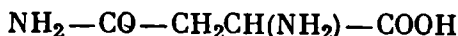
The molecules of *aspartic* (aminosuccinic) acid



and *glutamic* (α -aminoglutaric) acid



contain two carboxyls and one amino group; unlike the monocarboxylic amino acids, they exhibit distinct acidic reactions. *Asparagine*



and *glutamine*



which are present in plants are monoamides of the above acids. L(—)-Asparagine is especially widespread; it was found in the sprouts of asparagus. Considerable amounts of L(—)-asparagine are contained in etiolated (grown in darkness) plant sprouts; vetch sprouts contain no less than 28% of asparagine, and they also contain D(+)-

asparagine. It is noteworthy that the two antipodes have a different physiological effect: L-asparagine is tasteless, whereas D-asparagine is sweet. A difference in physiological effect is also observed among other optical antipodes. For instance, L(—)-nicotine (the natural product) is 2-3 times as poisonous as its antipode. According to Pasteur, the difference in physiological effect is due to the fact that the antipodes react with the asymmetric matter of living tissues to form compounds that are (with respect to each other) not antipodes, but diastereoisomers and for this reason have different physical and chemical properties.

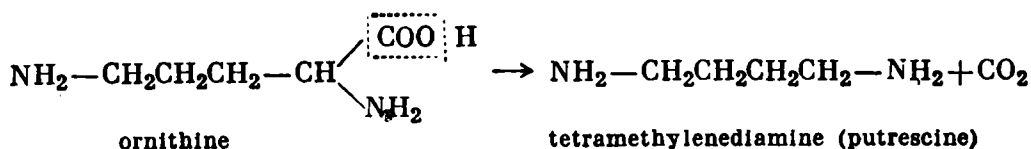
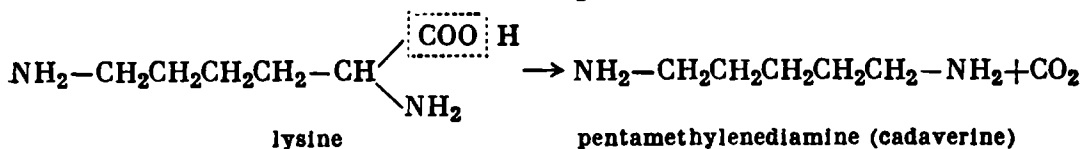
The most important among the other amino acids are *lysine*, or normal α,ϵ -diaminocaproic acid (2,6-diaminohexanoic acid)



and *ornithine*, or normal α,δ -diaminovaleric acid



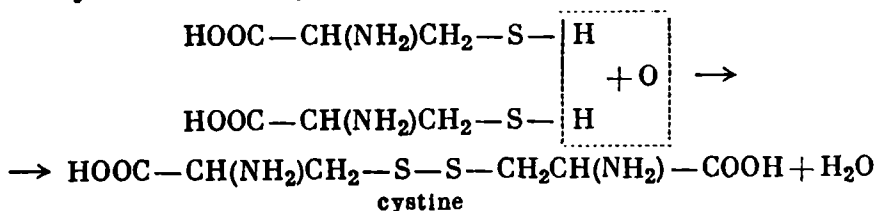
The molecules of lysine and ornithine contain two amino groups and only one carboxyl; accordingly, they have marked basic properties. Under the influence of putrefactive bacteria they lose a molecule of carbon dioxide and form ptomaines:



L-Lysine and L-ornithine are usually contained in the products of protein hydrolysis.

Ornithine is probably a secondary product of protein decomposition. The direct product of protein hydrolysis is arginine (p. 379), whose hydrolysis yields urea and ornithine.

Cysteine $\text{HS—CH}_2\overset{*}{\text{CH}}(\text{NH}_2)\text{—COOH}$ is a derivative of α -amino-propionic acid, in whose molecule one atom of hydrogen has been replaced by the —SH group. Oxidation by the oxygen of the air converts cysteine into cystine:



When proteins undergo hydrolysis the greater part of the sulphur they contain becomes part of L-cysteine or L-cystine. In certain diseases cystine forms calculi (commonly called stones) in the bladder and the kidneys.

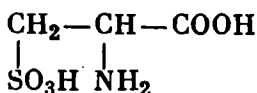
Serine $\text{HO}-\text{CH}_2\text{CH}(\text{NH}_2)-\text{COOH}$ is an oxygen-containing analogue to cysteine. It is contained in the hydrolysis products of sericine (silk glue); small amounts are formed when other proteins undergo hydrolysis.

Taurine $\text{NH}_2-\text{CH}_2\text{CH}_2-\text{SO}_3\text{H}$ is both an amine and sulphonic acid. It can be obtained from cysteine. Vigorous oxidation of cysteine

TABLE 13. Some α -Amino Acids and Corresponding Carboxylic Acids

Carboxylic acid	Amino acid
CH_3-COOH acetic acid	$\text{CH}_2(\text{NH}_2)-\text{COOH}$ glycine
$\text{CH}_3\text{CH}_2-\text{COOH}$ propionic acid	$\text{CH}_3\text{CH}(\text{NH}_2)-\text{COOH}$ α -alanine
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CHCH}_2-\text{COOH} \\ \diagup \\ \text{CH}_3 \end{array}$ isovaleric acid	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CHCH}(\text{NH}_2)-\text{COOH} \\ \diagup \\ \text{CH}_3 \end{array}$ valine
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CHCH}_2\text{CH}_2-\text{COOH} \\ \diagup \\ \text{CH}_3 \end{array}$ isocaproic acid	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CHCH}_2\text{CH}(\text{NH}_2)-\text{COOH} \\ \diagup \\ \text{CH}_3 \end{array}$ leucine
$\text{CH}_3\text{CH}_2\text{CHCH}_2-\text{COOH}$ $\quad \quad \quad $ $\quad \quad \quad \text{CH}_3$ β -methylvaleric acid	$\text{CH}_3\text{CH}_2\text{CHCH}(\text{NH}_2)-\text{COOH}$ $\quad \quad \quad $ $\quad \quad \quad \text{CH}_3$ isoleucine
$\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{COOH}$ succinic acid	$\text{HOOC}-\text{CH}_2\text{CH}(\text{NH}_2)-\text{COOH}$ aspartic acid
	$\begin{array}{c} \text{NH}_2-\text{C}-\text{CH}_2\text{CH}-\text{COOH} \\ \quad \\ \text{O} \quad \text{NH}_2 \end{array}$ asparagine
$\text{HOOC}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{COOH}$ glutaric acid	$\text{HOOC}-\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)-\text{COOH}$ glutamic acid
	$\begin{array}{c} \text{NH}_2-\text{C}-\text{CH}_2\text{CH}_2\text{CH}-\text{COOH} \\ \quad \\ \text{O} \quad \text{NH}_2 \end{array}$ glutamine
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\text{COOH}$ valeric acid	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)-\text{COOH}$ ornithine
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{COOH}$ caproic acid	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)-\text{COOH}$ lysine

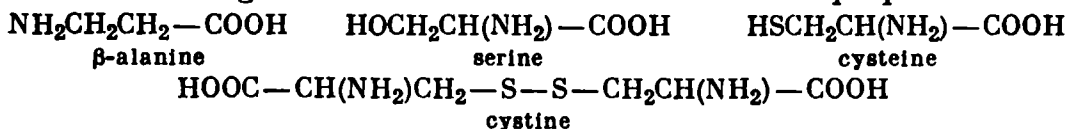
produces the sulphonic acid



which, when heated in a sealed tube, loses CO_2 and turns into taurine. Taurine was first discovered in the hydrolysis products of the bile of bulls (*taurus* in Latin means bull), the main constituent of bull's bile being taurocholic acid.

Table 13 gives the formulas of some of the amino acids and of the substances from which they are derived.

The following amino acids are also derivatives of propionic acid:



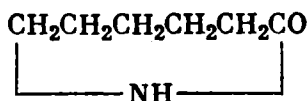
The physical properties of some of the natural amino acids are listed in Table 14.

TABLE 14. Physical Properties of Certain Natural Aliphatic Amino Acids

Amino acid	Melting point or decomposition temperature, °C	Optical activity	Solubility in water
Glycocoll	289-292	inactive	dissolves readily
L (+)-Alanine	297	2.7°	" "
L (-)-Serine	228 (decomp.)	-6.8°	" "
L (-)-Cystine	258-261 (decomp.)	222.4° (in hydrochloric acid solution)	almost insoluble without heating
L (+)-Valine	315	6.42°	dissolves very readily
L (-)-Leucine	337	-10.4°	1 : 45 (at 20°)
L (+)-Isoleucine . . .	280	9.7°	1 : 25.8 (at 15°)
L (+)-Arginine	228 (decomp.)	26.1°	dissolves readily
L (+)-Ornithine	(syrup)	16.8° (hydrochloride)	" "
L (+)-Lysine	224 (decomp.)	0.3° (hydrochloride)	" "
L (-)-Aspartic acid	270	6° (at 21.5°) (at higher temperatures is laevorotatory)	1 : 222 (at 20°)
L (+)-Glutamic acid	248	12.0°	1 : 100 (at 16°)
L (-)-Asparagine	236	-5.4°	3.1 : 100 (at 28°)
L (+)-Glutamine	—	6.45°	1 : 27.7 (at 18°)

Protein hydrolysis products include more complex amino acids: arginine (p. 379), phenylalanine (p. 461), tyrosine (p. 461), thyroxine (p. 461), proline (p. 379), tryptophane (p. 547), and certain others.

Epsilon-aminocaproic acid and its lactam



have lately acquired great practical importance. The acid does not occur in nature, but large quantities of it are synthesized and used for manufacturing capron, a synthetic fibre similar to nylon (p. 363).

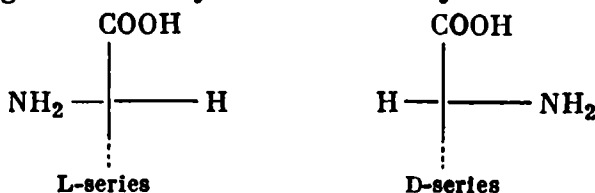
187. Designation of Stereoisomeric Molecules Containing Amino and Hydroxy Groups. Mirror isomers were originally designated by the terms “right-handed” and “left-handed”. But these terms are arbitrary, since objects or molecules are not “right-handed” or “left-handed” as such.

For many classes of compounds configurations were then chosen that were assumed to be “right-handed” and were designated by the letter D (from *dexter* meaning right), while their mirror images were assumed to be “left-handed” and were designated by the letter L (from *laevo* meaning left).

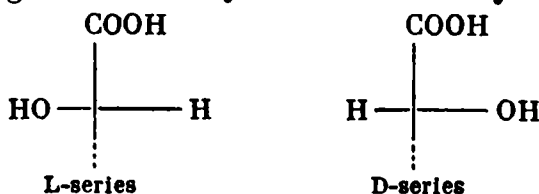
If a molecule has only one asymmetric centre, the arrangement of the atoms in the molecule is described accurately by the designations D and L. But if a molecule has several asymmetric centres, the letters D and L describe the configuration of only one asymmetric centre, which is considered the “key” one.

For the families of α -hydroxy and α -amino acids it is the asymmetric centre of the carbon atom (i.e., the one closest to the carboxyl) that is regarded as the “key” centre. For the families of hydroxy aldehydes and hydroxy ketones it is the asymmetric atom furthest from the carbonyl that is regarded as the “key” one. The configuration of the functional derivatives is designated by the same symbol as the configuration of the initial compounds.

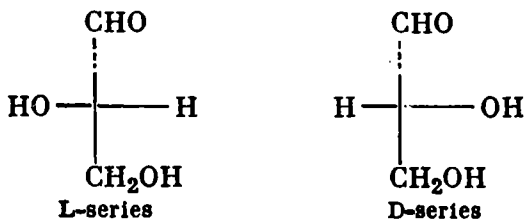
The following is the “key” to the family of amino acids:



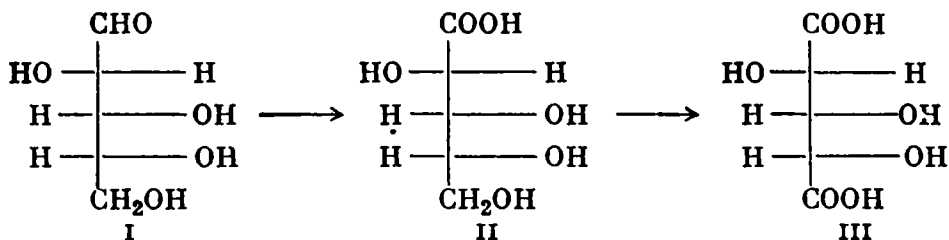
The following is the “key” to the family of hydroxy acids:



The following is the "key" to the family of hydroxy aldehydes:

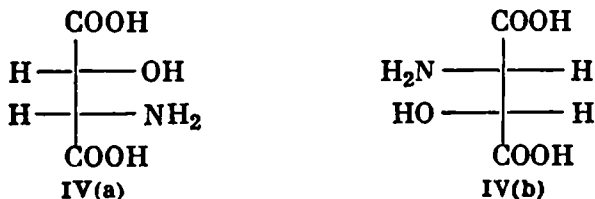


The asymmetric "keys" at first introduced some order into the nomenclature of compounds with several asymmetric centres, specifically into the nomenclature of the aldoses and ketoses. In many cases these notions have retained their value to this day. But very soon, in passing from one chemical to another, there arose misunderstandings, which have still not been resolved. For example, the oxidation of D-arabinose (I) yields the corresponding D-arabonic acid (II) and then trihydroxyglutaric acid (III) (according to the "key" of the hydroxy aldehydes they belong to the D-series):



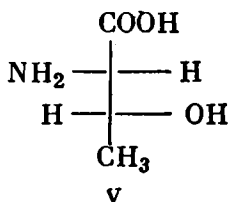
It is easy to see that these very same compounds should, according to the "key" to the α -hydroxy acids, be referred to the L-series. As for trihydroxyglutaric acid (III), it can, according to either "key", be referred to either the D- or the L-series.

Matters become even more complicated if a compound has several asymmetric centres relating to different "keys". A case in point is amino hydroxysuccinic acid, which can be referred either to the D-hydroxy acid series (IVa) or to the L-amino acid series (IVb):



Equally confusing is the case of the amino sugars and the hydroxy amino acids, which occur extensively in nature. Their mutual conversions are also difficult to describe in terms of D and L symbols. For example, 2-amino-3-hydroxybutyric acid (V) can be referred to the D-series, according to the hydroxy aldehyde "key", and to

the L-series, according to the amino acid "key":



To eliminate confusion, the additional indices *g* and *s* were introduced for such compounds. The symbols D_g and L_g indicate that the configuration has been defined in the hydroxy aldehyde "key" (*g* for glyceraldehyde or glucose), while D_s and L_s indicate that the configuration has been defined in the hydroxy amino acid "key" (*s* for serine).

The method of "keys" thus requires that ever new "keys" and rules be introduced to define the D- and L-series for every new group of compounds. As a result, a simple system, expedient for a relatively small number of compounds, becomes cumbersome and contradictory as the compounds grow more complicated. This is a typical instance of how the evolution of content makes it necessary to evolve a new, more advanced form.

Such a form, in the opinion of the authors of the present book, is the "rho-sigma" system (p. 151).

When we discussed the isomers of alcohols, hydroxy acids, and hydroxy aldehydes, it was pointed out that a graphic picture of the spatial structure of molecules could be preserved by means of the " ρ - σ " designations. This system is also of help when the "key" system is helpless. In this way the above-mentioned 2-amino-3-hydroxysuccinic acid (IV) can be called 2σ -amino- 3σ -hydroxysuccinic acid or, according to the Geneva nomenclature, 3ρ -aminobutanol-2 ρ -dioic-1,4 acid.

The "rho-sigma" system has the great advantage that it describes the configuration of each asymmetric centre. Therefore it can be used to describe all cases of mirror isomerism. The compounds mentioned in this section would have the following designations in the "rho-sigma" system:

I—pentatetraol- 2σ , (3,4) ρ , 5-al-1 or 2σ , (3,4) ρ , 5-tetrahydroxypentanal;

II—pentatetraol- 2σ , (3,4) ρ , 5-oic-1 acid or 2σ , (3,4) ρ , 5-tetrahydroxypentanoic acid;

III—pentanetriol- 2σ , (3,4) ρ -dioic-1,5 acid or 2σ , (3,4) ρ -trihydroxyglutaric acid.

The "rho-sigma" system makes it possible to designate configuration on the basis of either models or projection formulas and to reproduce either models or projection formulas. It must only be

remembered that in moving along the carbon atom chain as indicated on p. 151 the substituent to the left is designated by the letter ρ , while the substituent to the right is designated by the letter σ . This means that in the commonly used vertical projection of hydroxy acids, amino acids, and sugars the designation ρ will be equivalent to a D-configuration, while the designation σ will be equivalent to an L-configuration.

A detailed description of the "rho-sigma" system and its various applications can be found in the special literature.

Protein Substances

188. Proteins in Nature. Protein substances, or simply proteins, are present in all plant and animal organisms. They are the main constituent of protoplasm, occur in the blood, the milk, muscles, cartilages of animals, and account for the bulk of a chicken's egg. There are also proteins in hair, claws, horns, skin, feathers, wool, and silk. The animal organism is richer in proteins than the plant organism. In plants proteins occur in the protoplasm, the cell nucleus, the cell sap, and in seeds, but it is cellulose that forms the bulk of a plant.

Proteins are built up by plants with nitrogen derived either from salts in the soil or, as in the case of legumes, from the atmosphere. Syntheses of this type are beyond the reach of animals, which get their proteins ready-made by eating plants or other animals. Throughout the lifetime of an organism its protein constituents continuously undergo processes of decomposition and oxidation, and proteins are therefore an essential component of its food.

Nearly all proteins contain five elements: carbon, hydrogen, oxygen, nitrogen, and sulphur; some highly important proteins in addition to this contain phosphorus.

The contents of these elements in proteins vary within the following ranges (in %):

carbon	50-55	oxygen	19-24
hydrogen	6.6-7.3	sulphur	0.2-2.4
nitrogen	15-18		

There are proteins in which the sulphur content reaches 5%. On the other hand, the proteins in fish spermatozoa contain no sulphur at all; they are called *protamines*.

One of the proteins of the blood—haemoglobin—contains iron (0.3-0.5%). Finally, there are also proteins containing iodine and other halogens.

189. Properties of Proteins. Proteins are high-molecular non-volatile compounds, which do not dissolve in common solvents; the proteins that do dissolve in water give colloid solutions. Burning chars proteins, producing the characteristic odour of burned horn.

The following colour tests are ordinarily used to detect proteins.

Xanthoproteic* Reaction. When concentrated nitric acid is added to a protein it produces a yellow colour. The yellow stains that form on the skin when one handles concentrated nitric acid carelessly are the result of a xanthoproteic reaction with the proteins of the skin.

Biuret Reaction. This test consists in treating a solution of the protein with sodium hydroxide and adding a few drops of dilute cupric sulphate. This produces a violet colour. The reaction is often used for the qualitative detection of proteins.

Upon heating, as well as under the influence of many reagents, proteins experience complex changes called denaturation. This prop-

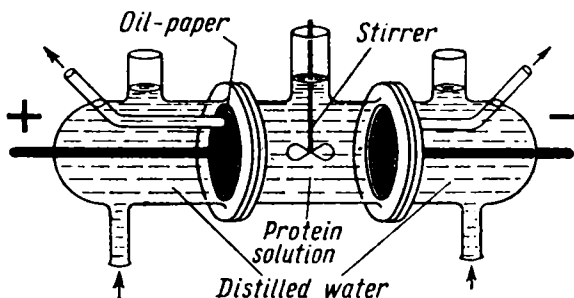


Fig. 56. Set-up for electrodialysis.

erty of proteins greatly hampers the study of their chemical structure. What is more in nature proteins always occur in complicated mixtures, and their isolation and purification are therefore fraught with great difficulties. Special methods have been evolved for such compounds, methods not resorted to in dealing with common organic substances.

Water-soluble proteins are usually isolated and purified by fractional salting-out by means of solutions of neutral salts: NaCl , Na_2SO_4 , MgSO_4 , $(\text{NH}_4)_2\text{SO}_4$, etc. The protein fractions separated in this way are freed from the salts by dialysis through a semi-permeable membrane (parchment, collodion film, tanned gelatin, etc.), which readily permits the passage of salts and other low-molecular substances, but retains the high-molecular proteins. *Electrodialysis* is likewise often used.

Fig. 56 shows a set-up for electrodialysis. An aqueous solution of the protein with the salts is poured into the central vessel; distilled water is passed slowly through the side vessels, separated from the central one by parchment membranes. The salt ions are quickly carried through the membranes to their respective electrodes. Isolated and purified proteins can even be obtained in the crystalline state.

* The Greek word *xanthos* means yellow

It is practically impossible to determine the molecular weight of proteins by conventional methods based on measuring the change in vapour tension, the elevation of the boiling point, or the depression of the freezing point of solutions. In most cases special methods are used, methods evolved for investigating high-molecular substances: estimation of the diffusion rate, determination of solution viscosity, ultra-centrifuging, etc.

Chemical techniques can also be used in some cases. This is illustrated by the case of casein, a protein isolated from milk. It has the following composition (in %):

Carbon	53.13	Nitrogen	15.78
Hydrogen	7.06	Sulphur	0.80
Oxygen	22.37	Phosphorus	0.86

There are thus 0.80 weight unit of sulphur in 100 weight units of casein. Since it is known that the sulphur in casein is in the form of a cystine molecule residue $[-OC-CH(NH_2)-CH_2S]_2$, the protein molecule has got to contain not less than two sulphur atoms, i.e., 64 weight units. Consequently, the molecular weight of casein may be determined from the proportion:

$$0.80 - 100$$

$$x = \frac{100 \cdot 64}{0.80} = 8,000$$

$$64 - x$$

If, however, we assume that the casein particle contains two cystine residues, the molecular weight will be $8,000 \times 2 = 16,000$. This value is of the same order as that obtained when the molecular weight is determined by physical methods. The molecular formula of casein is therefore $C_{708}H_{1130}O_{224}N_{180}S_4P_5$.

The molecular weight of egg albumin ("egg white") estimated by ultra-centrifuging is about 34,000; of haemoglobin (from blood), about 68,500. There are proteins with even higher molecular weights.

This makes it clear how complicated is the structure of these huge molecules and how difficult the task of determining that structure, let alone systematically synthesizing compounds analogous to proteins.

Proteins can be divided into two large groups: 1) *simple proteins* and 2) *conjugated proteins*. Careful hydrolysis breaks up conjugated protein molecules into simple protein molecules and non-protein molecules.

190. Simple Proteins. The simple proteins can be divided into several subgroups on the basis of some of their characteristic properties.

1. *Albumins*. These are soluble in water, coagulable by heat, neutral, and relatively difficult to precipitate by salt solutions.

Examples: ovalbumin (the chief protein constituent of the white of a chicken's egg), serum albumin, the albumin of muscle tissue, and lactalbumin. The latter, like casein, is a protein constituent of milk; the skin that forms on boiled milk also consists of lactalbumin.

Serum albumin is used industrially in the manufacture of printing paper and in calico printing. Like fibrinogen, it is obtained at slaughter-houses from the blood of animals. On leaving the blood vessels, fibrinogen coagulates to form fibrin. More efficient separation of the fibrin is achieved by whipping blood. The fibrin in this case forms white threads; the residue is a liquid, which is red owing to the red corpuscles in it. Centrifuging removes the corpuscles and produces serum. When the serum is evaporated carefully, crystals of albumin form in it.

2. *Globulins*. These are soluble in very weak salt solutions, but not in water. More concentrated salt solutions tend to precipitate them again; precipitation commences at a lower concentration than is necessary to precipitate albumins. The globulin proteins are very weak acids. Examples are fibrinogen, serum globulin of the blood, muscle tissue globulin, and egg white globulin. Egg white, the blood, and muscle tissues thus contain both globulins and albumins. Milk, on the other hand, contains practically no globulins. Many vegetable proteins likewise consist of globulins.

3. *Histones*. These are proteins with a basic reaction. They occur as nucleoproteins (p. 359) in leucocytes and the red corpuscles of the blood.

4. *Protamines*. These proteins do not contain sulphur, have relatively pronounced basic properties, and yield crystalline salts. They occur in the form of nucleoproteins in the spermatozoa of fish. Some scientists regard them as the simplest of all proteins.

5. *Prolamines*. These proteins are contained in the seeds of various cereals. Their remarkable property is their solubility in 80% alcohol. A representative of these proteins is *gliadin*, which is the chief constituent of gluten. Gluten is easily prepared from wheat: a handful of flour should be mixed into dough, wrapped in muslin, and washed in running water. The stretching, dirty yellow residue will be gluten.

Wheat gluten is a mixture of various proteins, with the above-mentioned gliadin predominating. The other proteins in gluten do not dissolve in alcohol.

6. *Scleroproteins* (Formerly *Albuminoids*). Insoluble proteins, which make up the external tissues of the animal body and are found in the skeletal and connective tissues. Examples are keratin, collagens, elastin, and fibroin.

Keratin is the principal constituent of hair, horns, hoofs, nails, feathers, and the top layer of the skin. The shell of a chicken's

egg consists of lime and keratin. If the lime is dissolved in acid, there remains a soft skin consisting of keratin; the skin underneath the egg shell likewise consists of keratin. Chemically keratin is rich in sulphur.

Collagens are exceedingly widespread in animal organisms. They make up the connective tissues and are contained in the cartilages. The bones of vertebrates consist of inorganic substances (calcium phosphate and carbonate), fat, and collagens.

When boiled with water or treated with superheated steam, collagens form a glue. If the fat is extracted from bones and they are treated with acid to dissolve the calcium phosphate, there remains a protein called *ossein*. Treatment with superheated steam turns ossein too into a glue. Pure bone glue is called *gelatin*. Especially pure gelatin is obtained from fish-sound by boiling it with water.

Elastin is a constituent of tendons and other elastic connective tissues.

Threads of raw silk consist of the protein called *fibroin*, which is covered with another protein; this other protein, *sericine*, plays the part of silk glue. Boiling with water frees the silk from the glue, which passes into the solution.

191. Conjugated Proteins. 1. *Phosphoproteins* contain phosphorus. Unlike protamines, which, as mentioned above, have basic properties, phosphoproteins are distinctly acidic.

The most representative phosphoprotein is *casein* of milk. Its acidity is so pronounced that it decomposes carbonates with the evolution of carbon dioxide. Casein dissolves in weak solutions of alkalis, forming salts with them. In milk, for example, it is contained in the form of its calcium salt. Casein salts are called caseinates.

When heated, casein does not coagulate. Treatment of caseinates with acids precipitates casein in the free state, which accounts for the turning of milk when it goes sour. The lactose of the milk in this case is converted, by the bacteria causing lactic fermentation, into lactic acid, and the acid precipitates the casein from its calcium salt in the form of a jelly-like mass. Cottage cheese is prepared by heating this mass to 35-40°.

The action of rennet enzymes upon milk causes casein to undergo a considerable change and turns it into insoluble paracasein, which is thrown down in the form of a clot. Subsequent treatment of the clot produces a cheese consisting primarily of paracasein. In making such cheeses, which, as distinct from the sour milk cheeses, are called rennet cheeses, it is customary to use an enzyme extract from the rennet bag of a calf.

Casein is used to make a hard horn-like plastic called *galalith*. This is manufactured by mixing the casein with water, dyes, and

fillers, compressing them under pressure, and treating the resulting plates with formalin. Casein contains phosphorus in the form of a phosphoric acid ester.

Another phosphoprotein is *vitellin* of egg yolk.

2. *Nucleoproteins* are constituents of cell nuclei. Careful hydrolysis breaks them up into a simple protein and a nucleic acid.

Nucleic acids are highly complex substances; they are decomposed by hydrolysis to phosphoric acid, carbohydrates, and nitrogen-containing organic substances of the pyrimidine and purine groups.

3. *Chromoproteins* are compounds of proteins and coloured substances. The most thoroughly studied of the chromoproteins is *haemoglobin*, the colouring matter of the red corpuscles of the blood. Haemoglobin combines with oxygen to form oxyhaemoglobin, which gives up its oxygen to other substances, thereby reverting to haemoglobin. Haemoglobin plays a very important part in the life of man and animals: it carries oxygen from the lungs to the tissues. The *oxyhaemoglobin* formed in the lungs is circulated by the blood through the body and gives up its oxygen to promote oxidation processes in the organism. In addition to this, haemoglobin in conjunction with the blood plasma regulates the pH of the blood and the circulation of carbon dioxide in the organism.

A characteristic feature of haemoglobin is its ability to combine with carbon monoxide, following which it is no longer able to combine with oxygen. This accounts for the poisonous action of carbon monoxide.

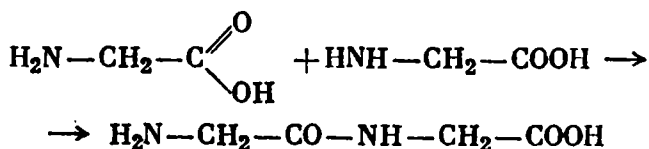
Haemoglobin is a compound of the protein *globin* and the colouring matter *haemochromogen*. Outside the organism haemoglobin is converted by the action of the air into *methaemoglobin*, in which the bond with the oxygen is stronger than it is in oxyhaemoglobin. Glacial acetic acid decomposes methaemoglobin to globin and *haematin* $C_{34}H_{32}O_4N_4Fe(OH)$. The treatment of methaemoglobin with the same reagent, but in the presence of NaCl, produces haematin hydrochloride, or *haemin* $C_{34}H_{32}O_4N_4FeCl$. Haemin forms characteristic reddish-brown platelets, and this makes it possible to detect the presence of blood in stains even after the passage of several years. Haematin is very similar to haemochromogen, but nevertheless differs from it.

4. *Glycoproteins*. Some of the proteins of this group occur in the mucous discharges of animal organisms and account for the ability of these discharges to stretch into threads even when comparatively highly diluted. These proteins form in the submaxillary gland (one of the salivary glands), the liver, and the glands of the stomach and intestines. Other glycoproteins are contained in the cartilages, in egg white, in the vitreous humour of the eye, etc. The glycoproteins studied have been found to be compounds of proteins and substances

containing certain carbohydrate derivatives, sulphuric-acid, and acetic-acid radicals.

192. Some Idea of the Chemical Structure of Proteins. As has been pointed out repeatedly, the carbon-carbon bonds in organic molecules are the most stable to chemical reagents. The heating of the substance with aqueous solutions of acids or alkalis as a rule fails to rupture these linkages; hydrolysis usually ruptures the bonds at the oxygen or the nitrogen, e.g., the hydrolytic decomposition of esters (such as fats) or amides. Proteins, upon hydrolysis, break up in the final analysis to α -amino acids. If a protein consists only of α -amino acids, it is a *simple protein*. But there are also, as we have seen, conjugated proteins, which incorporate the radicals of compounds belonging to other classes of organic and inorganic compounds.

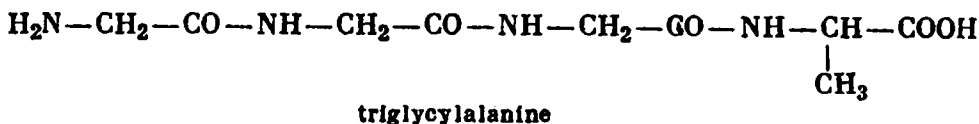
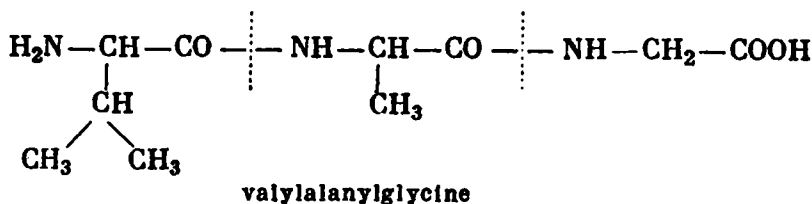
What are the principal forms of linkage between the amino acids in the complicated protein molecule? As far back as 1891 A. Danilevsky put forward the idea that these were amide linkages formed by the carboxyl of one amino acid molecule and the amino group of another:



Bonds of this kind are called *peptide linkages*. They can connect 2, 3, 4, . . . identical or different α -amino acid radicals into dipeptides, tripeptides, tetrapeptides, etc. Such compounds are called *polypeptides*.

This idea was later proved to be correct by Hofmeister and Fischer (1902).

Examples of compounds with peptide linkages are:



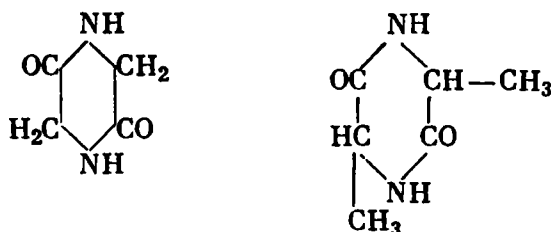
etc.

At one end of the polypeptide chain there is an amino group; at the other end, a carboxyl group.

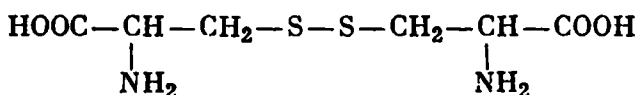
Quite recently chemists achieved the complete synthesis of several highly complicated natural polypeptides, which are biologically

important. They include the hormones: insulin, which consists of 51 amino acid residues, and oxytocin.

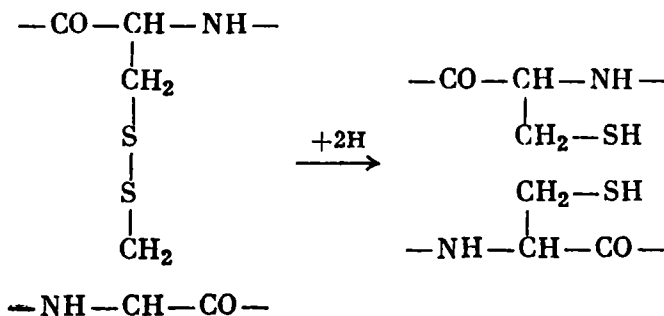
As distinct from linear chains of amino acids, some natural substances contain chains forming cyclic "anhydrides". The simplest of these *cyclopeptides* are the *diketopiperazines*. Their presence in proteins, assumed by N. Zelinsky and by E. Abderhalden, has not been confirmed. There are, however, natural cyclopeptides whose rings consist of many residues of different amino acids. These include the antibiotic gramicidin (p. 552) and the hormone oxytocin.



A very substantial part is played by the disulphide bond, which is formed by the linking up of the cysteine residues through the sulphur:



The peptide chains can in this way be "threaded together" by disulphide bridges. The peptide linkage is ruptured by hydrolysis; the disulphide, by reduction:



It is probable that the hydroxyl groups of the α -amino- β -hydroxy acids [$\text{HO}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$ —serine] also play some part in the formation of ester-type chains. This however has still not been fully established.

Apart from these purely covalent bonds, association forces* also operate between the polypeptide chains and the cycles.

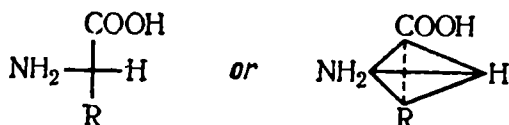
It should not be forgotten that the amino acid constituents of natural proteins include monoamino dicarboxylic acids and diamino

* Similar to the forces responsible for the association, say, of alcohols.

monocarboxylic acids. An excess of the former increases the acidity of the protein. Proteins that are basic contain a certain surplus of diamino acids.

Several typical reactions of proteins are due to the presence of phenylamino acids (tyrosine—p. 461) and amino acids with heterocyclic systems, such as tryptophane (p. 547) and proline (p. 540).

All the α -amino acids (except glycocoll) have an asymmetric carbon atom; it is noteworthy, moreover, that the amino acids in natural proteins belong to the L-series:



The study of the amino acid composition of proteins is a very difficult task, as it involves separating a mixture of substances of similar composition and structure. A notable advance in this problem was achieved by applying the method of chromatographic adsorption invented by the Russian botanist M. Tsvet.

The method is described on p. 542. Here we shall confine ourselves to saying that the most widespread technique in studying the hydrolysis products of proteins is the filter paper process of separation chromatography.

Proteins are distinguished by a great variety of chemical functions: they form compounds with non-protein substances and very readily (in natural conditions) undergo decomposition and aggregation. For example, protein hydrolysis requires the sustained action of mineral acid solutions at a high temperature, but organic catalysts, or ferments, make such decomposition possible at 20–40° within a short period of time. The action of organic catalysts is exemplified by the processes of digestion under the influence of digestive enzymes and by numerous metabolic processes.

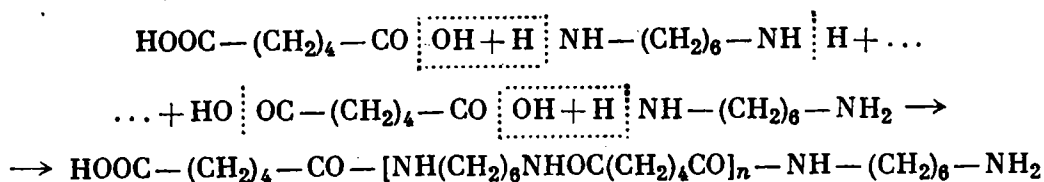
193. Synthesis of Proteins. As stated above, proteins are made up of numerous α -amino acid residues connected by amide, disulphide, and certain other systems of linkage. Modern organic chemistry has at its command a vast arsenal of various synthetic methods. Many clever and refined techniques have been suggested for preparing polypeptides of a certain predetermined structure. This has led chemists to tackle the artificial preparation of compounds similar in structure to the proteins.

But despite the efforts of many researchers, no substances identical to natural proteins have yet been prepared. The difficulty of the task is due not only to the physico-chemical properties of proteins, which hamper their preparation in pure form, but also to the tremen-

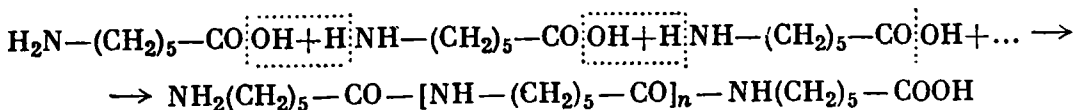
dous number of possible isomers. For example, even if each of the twenty hydrolysis products of a protein is represented in it by a single molecule, changes in their sequence can produce 2.3×10^{18} different isomers. If, in addition to this, it is taken into account that a protein molecule can contain not one, but several molecules of the same amino acid and that proteins can differ not only in structure, but also in the spatial configuration of the atoms, very many more naughts have to be added to the above figure. There can thus be an almost infinite variety of proteins. Nevertheless, the study of hydrolysis products provides us with a reliable means of gaining an insight into the structure of the protein molecule and makes it possible to solve the complex problem of synthesizing proteins.

194. Synthetic Fibre. Polyamide resins. The fibrous materials of animal origin (silk, wool, etc.) are proteins; their molecules consist of long chains of amino acids connected by amido linkage. Soluble proteins are suitable material for preparing artificial fibres by spinning solutions of the proteins (e.g., casein) under pressure through spinnerettes. Subsequent treatment with formaldehyde makes the threads insoluble in water.

Far more important, however, are the strong synthetic fibres of polyamide resins in which the components of the polymer are linked in the same way as the amino acids in a protein molecule (wool). The most important of these polymers industrially are: *nylon*, which is a product of the condensation of a large number of molecules (*polycondensation*) of adipic acid and hexamethylenediamine



and *capron (perlon)*, which is a polycondensation product of ϵ -aminocaproic acid*:



By extruding molten nylon or capron under pressure from spinnerettes with 0.25μ diameter orifices, it is possible to obtain a fibre stronger than other natural or artificial fibres. Polyamide resin fibres are used in the manufacture of car and aeroplane tyres, strong and non-rotting fishing nets, etc.

* As demonstrated by I. Knunyants, capron is best prepared by heating to a high temperature the lactam of ϵ -aminocaproic (6-aminohexanoic) acid, which polymerizes and yields capron.

Capron and nylon fibres are used on a particularly large scale in the manufacture of knitwear. It is common knowledge that fabrics made from these synthetic resins should not be pressed with a very hot iron, as they tend to melt when heated.

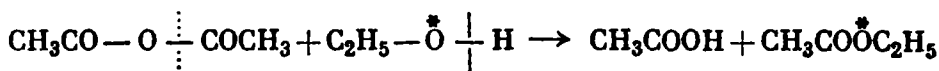
Soviet chemists recently produced a new type of fibre, *enant*, which is more resistant to light and more elastic than capron. The raw materials for manufacturing enant are ethylene and carbon tetrachloride.

The polyamide resins are good insulators, which accounts for their applications in electrical engineering.

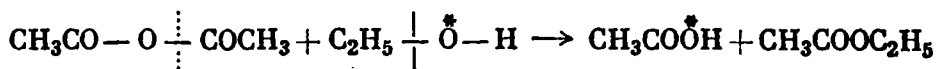
195. Tagged Atom Techniques. The tremendous advances in the physics and chemistry of the stable and radioactive isotopes of many elements offer boundless possibilities for studying many problems in organic chemistry, biochemistry, and medicine, not to mention other fields. The high-precision techniques of detecting and estimating isotopes make it possible to solve problems that defied conventional chemical methods. Work of this kind in many cases requires organic substances whose molecules have been made to contain the ordinary and radioactive (rad) isotopes: deuterium (D), tritium H^3 (rad), heavy oxygen O^{18} , sulphur S^{34} or S^{35} (rad), C^{14} (rad), P^{31} (rad), etc. Since compounds containing tagged atoms are very expensive and in some cases their handling involves a health hazard, the chemist must be highly proficient in working with very minute quantities of substances, often with the observance of special precautions. This, however, is not preventing chemists from pursuing such research with the greatest vigour.

Here are a few examples of the application of tagged, or labelled, atom techniques.

The reaction between acetic anhydride and ethyl alcohol, which yields ethyl acetate and acetic acid, permitted of two interpretations:



or



By using the labelled oxygen atom O^{18} , A. Brodsky and N. Dedusenko (1940) proved the former mechanism to be actually correct.

The mechanism of the formation of an ester from an alcohol and acid was established in the same way.

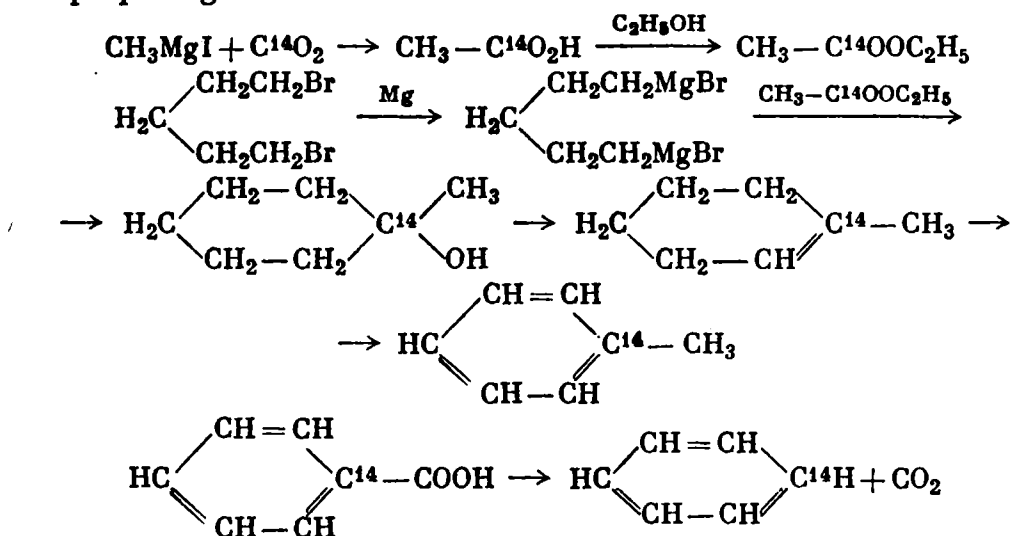
The quality of silk is known to depend largely upon an extremely thin coating of sodium oleate, which is applied in the process of production. If this coating is applied unevenly, the subsequent dyeing is likewise uneven and the quality of the weaving suffers drastically. The uniformity of the sodium oleate coating can be controlled by

introducing radioactive sodium into the salt. When the layer of sodium oleate is too thin, the radioactivity drops below the control figure, whereas a thick layer sends the radioactivity up. This makes it possible to control output quality.

In 1940 A. Vinogradov and R. Teis demonstrated that the oxygen given off by plants in the process of photosynthesis is oxygen that can be traced to water, but not to carbon dioxide. A. Kursanov found that plants can also assimilate carbon dioxide through their roots.

Highly interesting biochemical investigations have been carried out with the use of labelled acetic acid $\text{CD}_3\text{—C}^{14}\text{O}_2\text{H}$. A great deal of work has also been done in the study of metabolism by means of compounds containing radioactive phosphorus P^{31} . Use has been made of synthetic nitrogen-containing substances (urea, amino acids) with the stable nitrogen isotope N^{15} .

Certain sulphur-containing amino acids have been synthesized and used, such as $\text{CH}_3\text{—S}^{34}\text{—CH}_2\text{—CH}_2\text{—CH}(\text{NH}_2)\text{—COOH}$ (methionine). But it is various substances with the radioactive carbon isotope C^{14} that are used in organic chemistry and biochemistry on a particularly large scale. The initial substance for such syntheses is often C^{14}O_2 (from $\text{BaC}^{14}\text{O}_3$). Very many syntheses are carried out by means of the Grignard reaction: the preparation of acids, esters, ketones, alcohols, etc. Syntheses sometimes become highly important despite the fact that they could never conceivably be of practical value. For example, there are descriptions of the following procedure for preparing toluene and benzene:



The resulting compounds can themselves serve as initial substances in synthesizing many compounds needed for various types of research, such as drugs, and for the study of their behaviour in animal organisms, since the presence of a radioactive element (C^{14} , P^{31} , etc.) can be detected with great accuracy by proper physical methods.

Cyan Compounds

196. Cyan Compounds and Their Sources. Cyan compounds are substances containing the cyan radical CN; they can have either of two structures:

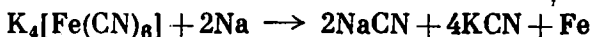


The simplest cyan compounds are cyanogen (CN)₂ and hydrocyanic, or prussic, acid HCN.

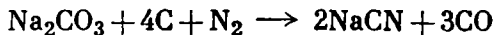
The term cyan is derived from the Greek word *kyanos* meaning azure. The radical was named so because it occurs in the blue dyes Prussian blue and Turnbull's blue.

One of the sources of cyan compounds is potassium ferrocyanide K₄[Fe(CN)₆], which crystallizes with three molecules of water: K₄[Fe(CN)₆] · 3H₂O. The crystals are also known as yellow prussiate of potash. In the past potassium ferrocyanide was prepared chiefly from slaughter-house waste (horns, hoofs, and blood) by fusing them with potash in the presence of iron filings. At present large amounts of this substance are prepared from used gas-purification matter (containing ferric hydroxide), which serves to purify lighting gas.

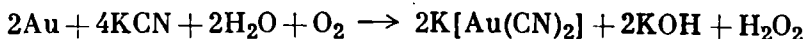
When potassium ferrocyanide is fused with metallic sodium, both potassium cyanide and sodium cyanide are formed:



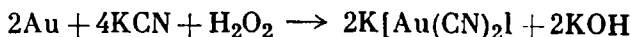
Sodium cyanide can also be prepared by other methods, for instance, by heating soda with coal in an atmosphere of nitrogen:



Sodium and potassium cyanides are white, crystalline, exceedingly poisonous substances. In the presence of atmospheric oxygen their aqueous solutions are capable of dissolving gold; for this reason they are used in large quantities for extracting gold from ores (the cyanide method):



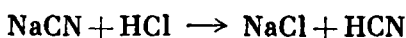
The resulting hydrogen peroxide takes part in forming a complex gold salt:



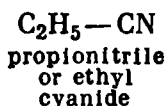
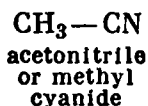
The gold can be isolated from this complex salt by various means, for example, by metallic zinc.

The metal cyanides are also used in gold, silver, and nickel electroplating. In organic chemistry potassium cyanide has many uses for syntheses. Recall, for example, the preparation of mono- and polycarboxylic acids, as well as hydroxy and amino acids, via the intermediate formation of nitriles and their subsequent hydrolysis (p. 206).

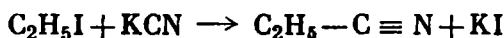
The action of acids upon potassium or sodium cyanide produces hydrocyanic acid HCN:



197. Nitriles: Their Preparation and Properties. Nitriles are substances in which an organic radical is linked to the carbon of the CN group:

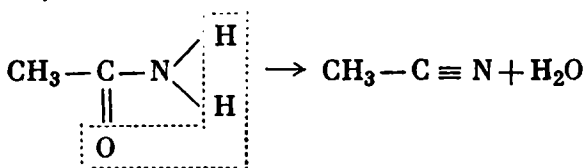


Nitriles can be prepared by the action of potassium cyanide upon alkyl halides:



The carbon chain is in this case extended by one link.

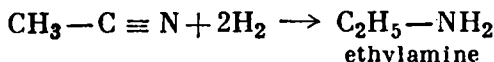
Another method of preparing nitriles is by removing water from acid amides by heating them with dehydrating agents (e.g., phosphoric anhydride):



Nitriles whose molecules contain less than fourteen carbon atoms are liquids, whereas the higher nitriles are solids. Nitriles have a characteristic odour resembling that of bitter almonds. They are poisonous, but much less so than hydrocyanic acid.

The two most important properties of nitriles are these:

1. When nitriles are reduced, the cyan radical adds hydrogen to become an amino group:



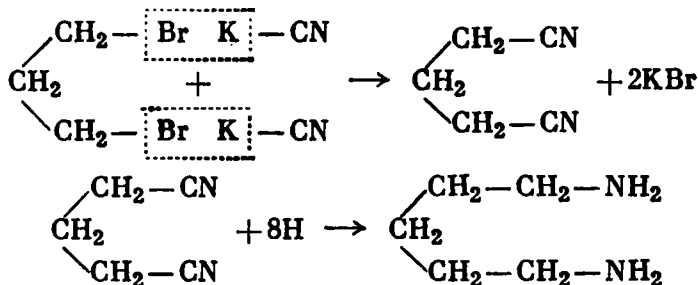
Reduction is conducted in an alcoholic solution by means of metallic sodium. The hydrogen evolved from the alcohol ruptures the second and the third bond between the carbon and nitrogen atoms; two atoms of hydrogen are added to each of them. This very impor-

tant method of reduction was suggested in 1880 by A. Vyshnegradsky, one of Butlerov's pupils.

The reaction of nitrile reduction establishes the structure of the diamines. For instance, the structure of pentamethylenediamine



is confirmed by the fact that it can be prepared from trimethylene bromide (1,3-dibromopropane) in the following way:



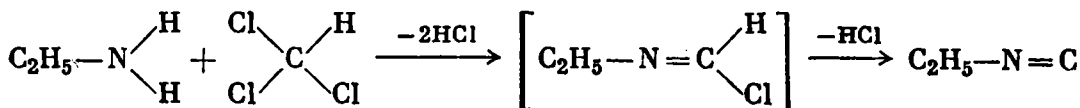
2. Acid and alkali solutions saponify nitriles to acids (p. 206).

198. Isonitriles. Isonitriles, or isocyanides, or carbylamines, are substances in which the organic radical is linked to the nitrogen of the CN group. One such substance is methylcarbylamine $\text{CH}_3-\text{N}=\text{C}$.

Isonitriles are formed with nitriles when alkyl halides are treated with cyanides. If potassium cyanide is used, the product consists chiefly of nitriles, but if silver cyanide is chosen, isonitriles result:

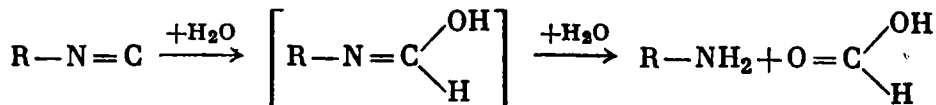


Another method of preparing isonitriles is by treating primary amines with chloroform and a caustic alkali:



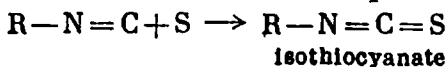
This reaction is used to detect primary amines, since the formation of even small quantities of isonitriles at once becomes apparent because of their characteristic and very repulsive odours.

The action of acids causes isonitriles to add water and break up into primary amines and formic acid:



This reaction proves that the hydrocarbon radical in isonitriles is linked to the nitrogen.

Isonitriles are capable of addition reactions; the addition takes place only at the carbon atom, for example:



The fact that addition takes place only at the carbon atom points to the specific character of the carbon atom in isonitriles.

The structure of isonitriles used to be represented by a formula with a "divalent" carbon atom. Nowadays, however, it is assumed that the carbon and the nitrogen in the isonitrile group are linked by something in the nature of a triple bond: two of the valencies are based on two "shared" electron pairs, while the third is derived entirely from the nitrogen atom. The carbon atom thus carries a free electron pair and has a negative charge, while the nitrogen atom is positively charged:



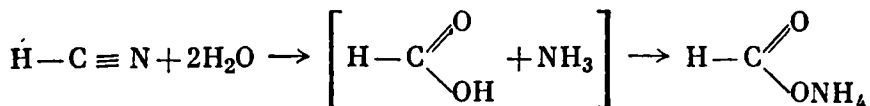
Isonitriles are liquids with lower boiling points than those of the isomeric nitriles. They are more poisonous than the nitriles and have repulsive odours.

199. Prussic Acid. Prussic, or hydrocyanic, acid HCN is a colourless liquid with an odour of bitter almonds (b.p. 25°). It is very slightly ionized in aqueous solutions and is extremely poisonous.

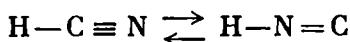
Prussic acid occurs quite often in plants, in both the free and the bound state. For instance, laurel-cherry leaves, bitter almonds, and the pits of peaches, apricots, plums and cherries contain the glucoside amygdalin $\text{C}_{20}\text{H}_{27}\text{NO}_{11} \cdot 3\text{H}_2\text{O}$, whose molecule upon hydrolysis breaks up into two molecules of glucose, a molecule of benzaldehyde, and a molecule of prussic acid:



Prussic acid is the nitrile of formic acid; when stored for a long time, its aqueous solution forms ammonium formate:



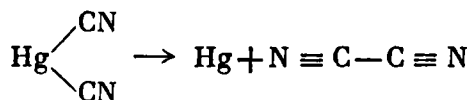
As stated earlier, the action of cyanides upon alkyl halides produces both nitriles $\text{R—C}\equiv\text{N}$ and isonitriles $\text{R—N}\equiv\text{C}$ simultaneously. For this and other reason prussic acid is considered to be a mixture of two tautomers with a high rate of tautomeric change:



The isonitrile modification is contained in prussic acid in small quantities.

Both in the free state and in the form of salts prussic acid has many applications in the national economy. Mixed with several other substances (arsenic chloride, tin chloride, chloroform) it was used in the world war of 1914-18 as a chemical warfare agent.

200. Cyanogen. Cyanogen $(\text{CN})_2$, often called dicyan, was first prepared in 1815 by Gay-Lussac, who heated mercuric cyanide:



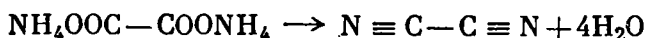
It can also be prepared by mixing solutions of cupric sulphate and potassium cyanide:



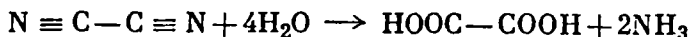
The $\text{Cu}(\text{CN})_2$ formed at first decomposes immediately to CuCN and free cyanogen. Small quantities of cyanogen form when nitrogen is passed through heated coal. By means of spectral analysis it has been established that cyanogen is present in the tails of comets.

Cyanogen is a colourless, highly poisonous gas, which condenses into a liquid at -20.7° and freezes at -34.2° .

It is also formed when ammonium oxalate is heated with dehydrating agents:



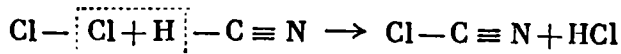
The action of dilute hydrochloric acid can saponify cyanogen to oxalic acid and ammonia (instead of them we, of course, obtain ammonium chloride and ammonium oxalate):



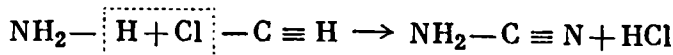
Cyanogen is thus the nitrile of oxalic acid.

Cyanogen exhibits a certain similarity to the halogens: the burning of potassium in an atmosphere of chlorine produces potassium chloride KCl , while its burning in cyanogen yields potassium cyanide KCN . Chlorine with potassium hydroxide yields KCl and KClO , while the passage of cyanogen through a KOH solution produces potassium cyanide KCN and potassium cyanate KCNO . Silver cyanide AgCN , like silver chloride, forms a white curdy precipitate which is insoluble in water, but dissolves in ammonia.

201. Cyanamide. The action of chlorine upon prussic acid produces cyan chloride $\text{Cl}-\text{C} \equiv \text{N}$ (b.p. 15.5°):

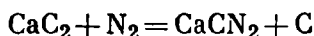


By treating a solution of cyan chloride in ether with ammonia we obtain cyanamide $\text{NH}_2-\text{C} \equiv \text{N}$:

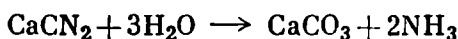


Cyanamide is a colourless, crystalline, deliquescent substance, which melts at $41-42^\circ$. The hydrogen in it is easily replaced by a metal.

A highly important compound is the calcium salt of cyanamide, calcium cyanamide $\text{CaN}-\text{C}\equiv\text{N}$, whose formula is usually written as CaCN_2 . Calcium cyanamide is prepared by treating heated calcium carbide with nitrogen:

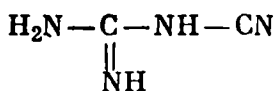


Water decomposes calcium cyanamide:

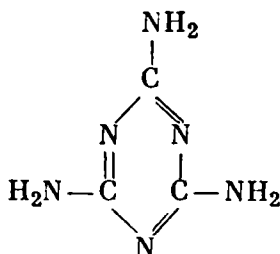


The decomposition of calcium cyanamide by heating it with water vapour under pressure is one of the possible ways of preparing ammonia, while the preparation of calcium cyanamide is one of the possible ways of fixing atmospheric nitrogen.

Thanks to this, calcium cyanamide was at one time used as a fertilizer, but was later replaced by other compounds (urea and ammonium nitre), which are more readily assimilated by plants. It is however still produced in large amounts for use as a cotton-plant defoliant and for the manufacture of certain nitrogen-containing compounds, such as



dicyandiamide

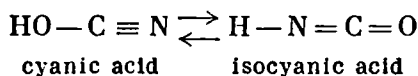
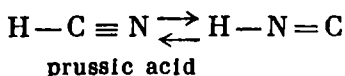


melamine

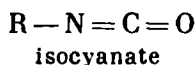
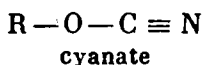
These two compounds are important in the production of certain surface-active agents and plastics.

202. Cyanic Acid. By fusing potassium cyanide with lead oxide we can obtain potassium cyanate, a salt of cyanic acid (the lead oxide in this case serves as an oxidizing agent). Cyanic acid is a volatile liquid which is very readily converted into solid polymers.

If we regard cyanic acid as an oxidation product of prussic acid, there must be two tautomeric forms of cyanic acid to correspond to the two tautomeric forms of prussic acid:



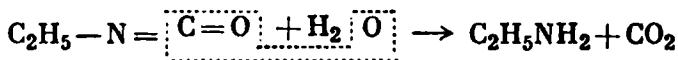
The two tautomeric forms of this acid have not been isolated, but their esters are known:



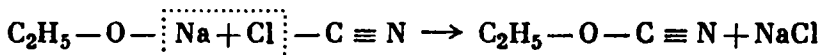
The isocyanates are liquids with an unpleasant odour. They are prepared by treating cyanic acid salts with alkyl halides:



The hydrocarbon radical in isocyanates is linked to the nitrogen. This is confirmed by the fact that when they are treated with alkali solutions, a primary amine and carbon dioxide are formed:



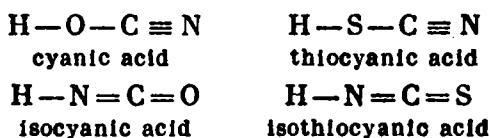
Cyanates are prepared by treating alcoholates with cyan chloride:



They polymerize at once to form trimers such as $(\text{C}_2\text{H}_5\text{OCN})_3$. The radical in these polymers is linked to the oxygen; their hydrolysis yields alcohols. Monomer cyanates have not been obtained.

203. Thiocyanic Acid. By boiling potassium cyanide with sulphur we obtain potassium thiocyanate KCNS , a salt of thiocyanic acid. The acid is a liquid, which is contained in rather considerable quantities in the fresh juice of onions.

Like cyanic acid, thiocyanic acid may be represented as having two tautomeric forms:



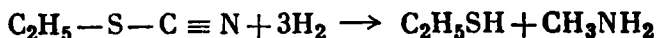
Esters of both isomeric forms are known:



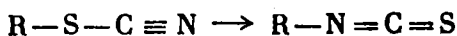
The thiocyanates are liquids with an odour of onions. They may be prepared by the action of alkyl halides upon thiocyanic acid salts:



The hydrocarbon radical in the thiocyanates is linked to the sulphur atom, which is confirmed by the formation of mercaptans and methylamine when these esters are reduced:

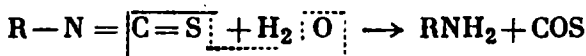


The isothiocyanates are called *mustard oils*. They are liquids with an extremely sharp smell. The mustard oils are prepared by heating thiocyanates:

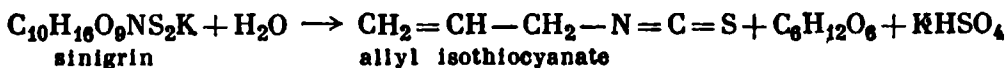


The radical in the isothiocyanates is linked to the nitrogen. This is evident from the fact that, when treated with sulphuric acid, these

esters add water and break up to form primary amines and carbon oxysulphide COS:



The mustard oils occur in the form of glucosides in the seeds and roots of certain plants. The plants usually also contain the enzymes that hydrolyze these glucosides. When such seeds are ground with water and kept in that state, mustard oils in the free state appear after a certain time. Black Indian mustard, for instance, contains the glucoside *sinigrin**, which is decomposed by enzyme action to glucose, allyl isothiocyanate, and potassium hydrogen sulphate:

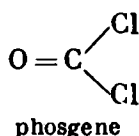
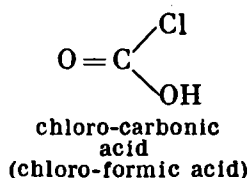
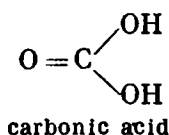


Allyl isothiocyanate has an extremely sharp smell; when it comes into contact with the skin, it causes a sensation of burning and produces blisters.

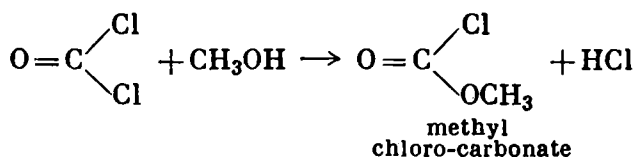
* Derived from *Sinapis nigra*, the Latin name of black mustard.

Carbonic Acid Derivatives

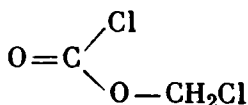
204. Carbonic Acid Chlorides. As a dicarboxylic acid, carbonic acid has two chlorides: the dichloride phosgene and the monochloride chloro-carbonic acid, which is also called chloro-formic acid:



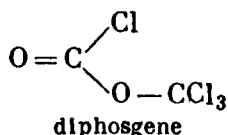
Chloro-Carbonic Acid and Its Esters. Chloro-carbonic (chloro-formic) acid can be regarded as a derivative of carbonic acid (in whose molecule a hydroxyl has been replaced by a chlorine atom) or as a derivative of formic acid $\text{H}-\text{CO}-\text{OH}$ (in whose molecule the hydrogen atom linked to the carbon has been replaced by chlorine). Chloro-carbonic acid has not been obtained in the free state, but its esters can be prepared by the interaction of phosgene with alcohols:



The chloro-carbonates (chloro-formates) are liquids with a pungent odour resembling that of phosgene; their vapours have a lachrymatory effect. The chlorination of methyl chloro-carbonate yields monochloromethyl chloro-carbonate (b.p. 106°)

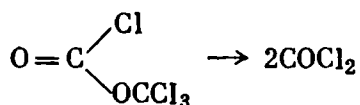


and trichloromethyl chloro-carbonate, or *diphosgene* (b.p. 127°)

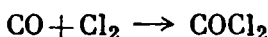


Both of these compounds were used in the war of 1914-18 as chemical warfare agents.

When heated, diphosgene decomposes, each molecule yielding two molecules of phosgene:



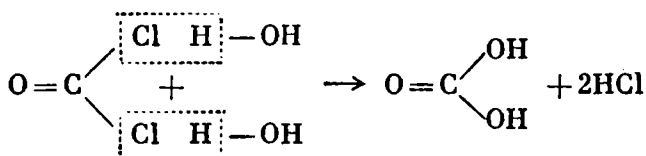
Phosgene COCl_2 was first prepared in 1811 by Davy, who exposed carbon monoxide and chlorine to sunlight (its name is derived from the Greek *phos* meaning light and *-genes* meaning -born; hence light-born):



Industrially phosgene is prepared by leading carbon monoxide and chlorine over activated charcoal at a high temperature. Phosgene is a gas, which under pressure or upon cooling condenses to a liquid (b.p. 8.2°). It has a strong, pungent odour.

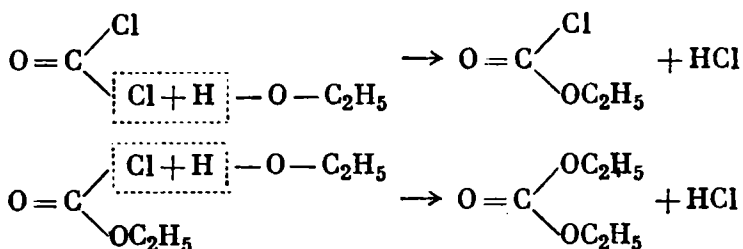
Phosgene is an asphyxiant; in the organism it affects primarily the lung tissues.

The reactions of phosgene are typical of acid chlorides. With water it forms carbonic acid and hydrochloric acid:



At ordinary temperature the reaction proceeds quite slowly.

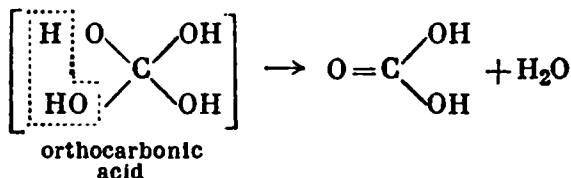
The action of alcohols upon phosgene produces chloro-carbonates and then carbonates:



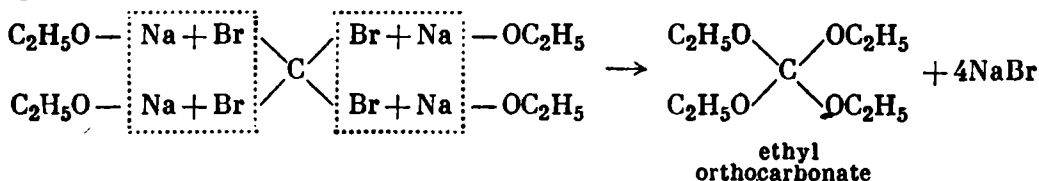
Phosgene is used in the aniline dye industry. In the war of 1914-18 it was used as a chemical warfare agent.

205. Carbonic Acid Esters. Carbonic acid esters can be prepared by the interaction of phosgene with alcohols. They are colourless liquids with a pleasant odour, which have a low solubility in water.

Chemists have also prepared esters of the hypothetical orthocarbonic acid:

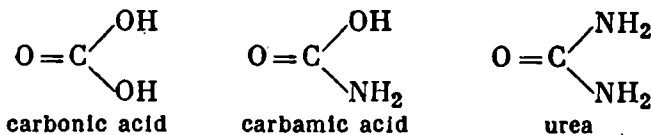


Esters of this acid may be prepared by the action of alcoholates upon carbon tetrabromide:

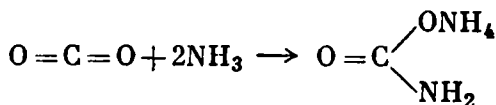


Ethyl orthocarbonate is a liquid; water decomposes it to alcohol and ethyl carbonate.

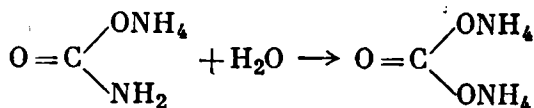
206. Nitrogen-Containing Carbonic Acid Derivatives. There are two amides corresponding to carbonic acid: a diamide known as urea, or carbamide, and monoamide called carbamic acid:



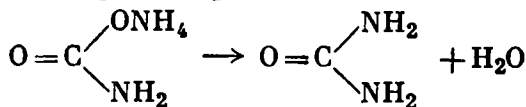
Carbamic acid is unknown in the free state, but its ammonium salt, ammonium carbamate, can be prepared by the reaction between carbon dioxide and ammonia:



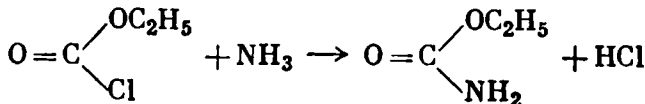
Interaction with water converts ammonium carbamate into ammonium carbonate:



Ammonium carbamate gives up water to become urea:



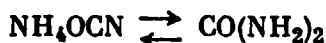
The esters of carbamic acid are called *urethans*. They can be prepared by the action of ammonia upon chloro-carbonates:



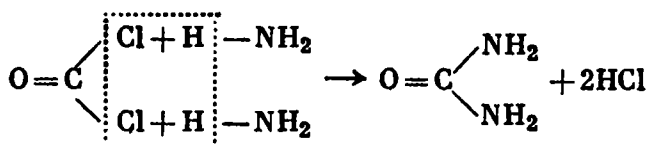
Urethans are crystalline substances. Some of them are used in medicine as soporifics and anaesthetics.

Urea $\text{CO}(\text{NH}_2)_2$ is the chief end product of the metabolism of proteins in mammal organisms. Large quantities of it are therefore contained in the urine of man and other mammals (about 2% of the human urine is urea). A human being excretes 20-30 g of urea a day.

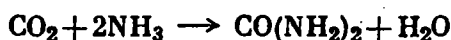
Synthetically urea was first prepared in 1828 by Wöhler*, who evaporated an aqueous solution of ammonium cyanate. The ammonium cyanate in this case isomerizes into urea, the reaction being reversible:



The structure of urea is made evident by its synthesis from phosgene and ammonia:



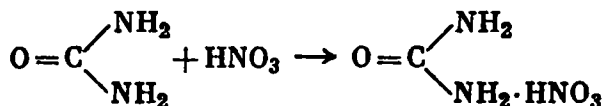
The industrial manufacture of urea, which is used extensively as a fertilizer, is based on heating a mixture of ammonia and carbon dioxide under pressure:



Urea forms flat prism-shaped crystals similar to the crystals of potassium nitre; it melts at 133° and is very soluble in water.

An unexpected property of urea was discovered recently: it was found that in the presence of a small amount of methyl alcohol the crystals of urea are capable of adsorbing paraffin hydrocarbons, alcohols, and halogen derivatives with unbranched hydrocarbon chains. Compounds with branched chains, on the other hand, are not adsorbed by urea. This is due to the specific structure of the urea crystals, which have "crystalline pores", so narrow that hydrocarbons with branched chains cannot penetrate them. A practical use to which this has now been put is the isolation of normal paraffins from oil products: after the liquid phase, containing isoparaffins, has been pressed off, the crystals are treated with water, which transfers the urea into the aqueous solution, while the hydrocarbon is separated.

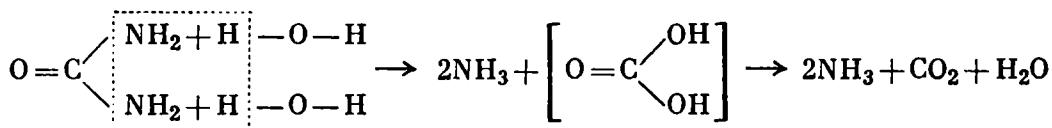
As an amide, urea reacts with acids to form salts, but only one amino group takes part in the reaction of salt formation:



* Friedrich Wöhler (1800-82), German chemist, was a pupil of J. Berzelius's. Wöhler's many investigations in organic chemistry included the synthesis of urea (1828), and the preparation and study of benzoyl derivatives (in collaboration with J. Liebig, 1832), and of uric acid.

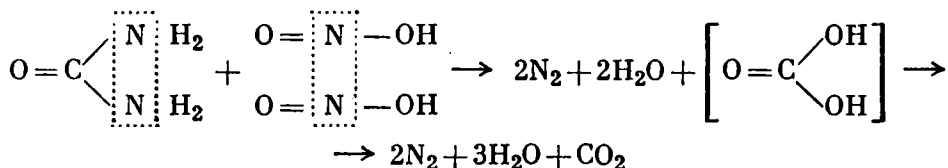
Urea nitrate dissolves in water with difficulty.

Upon heating with solutions of alkalis or acids, urea, like all amides, breaks up to form an acid and ammonia:

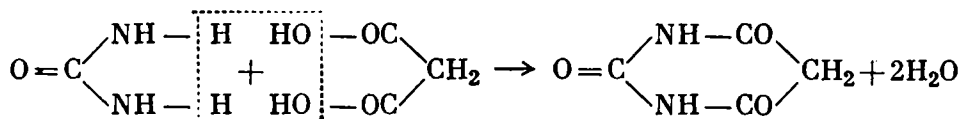


This decomposition is also brought about by *urease*, an enzyme found in the kidneys of mammals and in the seeds of many plants, for example, in soya beans.

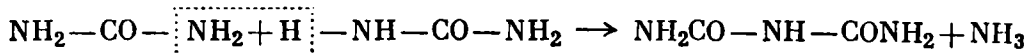
With nitrous acid, urea, like other amides, produces nitrogen and an acid:



Urea can react with acids, acid chlorides, anhydrides, and esters. When urea is treated with acetyl chloride, a hydrogen atom in one of the amine groups is replaced by the acetyl, with the formation of acetylurea (m.p. 217°). Upon heating with malonic acid, urea yields barbituric acid (crystals):

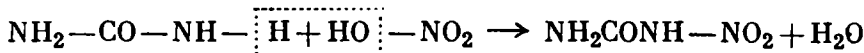


Heated above its melting point, urea gives off ammonia and turns into *biuret*:



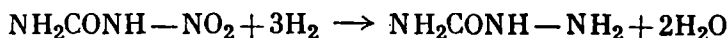
Biuret melts at 190°. In an alkaline solution with cupric sulphate, biuret gives a reddish violet colour.

Semicarbazide. When urea is treated with concentrated nitric acid in the presence of concentrated sulphuric acid, it yields nitrourea:



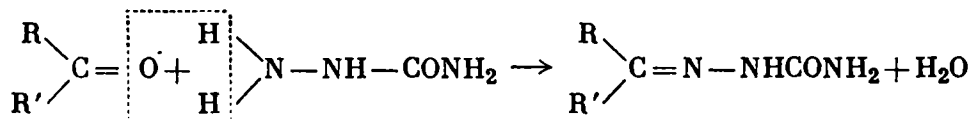
Nitrourea is a crystalline substance melting at 150° with decomposition.

Electrolytic reduction converts nitrourea into semicarbazide:



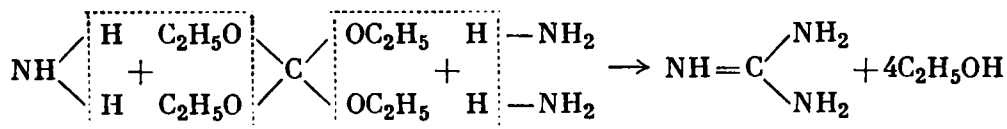
Semicarbazide is a crystalline substance melting at 96° . It forms salts, acting as a monoacid base.

With aldehydes and ketones, semicarbazide gives *semicarbazones*:

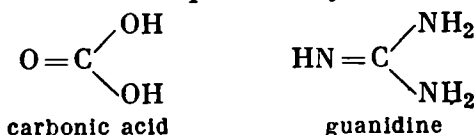


Semicarbazones crystallize readily; they are used to identify aldehydes and ketones, as well as to separate them from other substances.

Guanidine is formed by the action of ammonia on esters of ortho-carbonic acid:



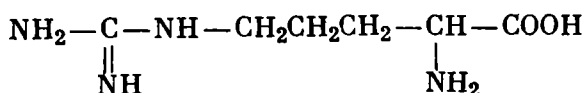
It can be regarded as a derivative of carbonic acid, in whose molecule two hydroxyls have been replaced by amino groups, while the carbonyl oxygen has been replaced by an NH group:



Guanidine is a colourless, crystalline substance. It is very hygroscopic, absorbs carbon dioxide from the air, forms salts, acting as a monoacid base, and exhibits pronounced alkaline properties.

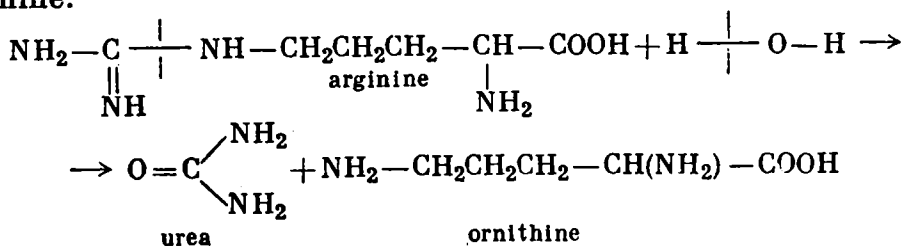
Among the derivatives of guanidine, two are highly important physiologically: arginine and creatine.

Arginine



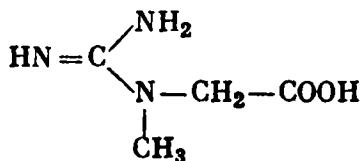
can be regarded as a derivative of α -aminovaleric acid, in whose molecule a hydrogen atom at the δ -carbon atom has been replaced by the guanidine residue. Arginine is α -amino- δ -guanidinevaleric acid, one of the chief products of the hydrolysis of many proteins. It occurs in the free state in the sprouts of plants.

When heated with alkalis, arginine decomposes to urea and ornithine:

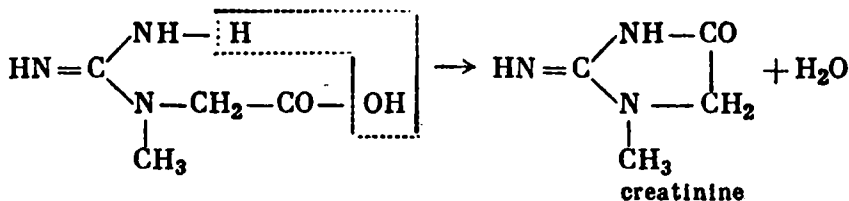


Such decomposition is also brought about by *arginase*, an enzyme present in the liver.

Creatine

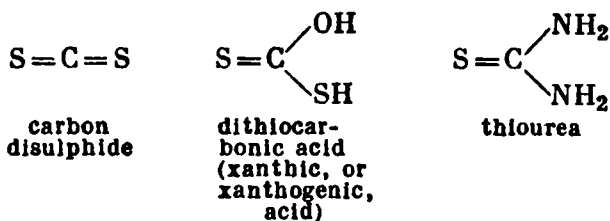


can be regarded as a derivative of acetic acid, in whose molecule a hydrogen atom has been replaced by a guanidine residue methylated at a nitrogen atom. Creatine is N-methylguanidinoacetic acid. It is present in the muscle fluid of vertebrates; it melts at 100° and has a bitter taste. When heated with dilute acids, creatine loses water to become *creatinine*:



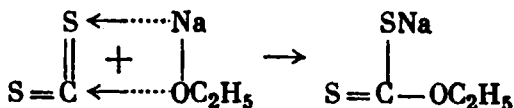
Creatinine is present in the muscle fluid and urine of animals, as well as in plants.

207. Sulphur-Containing Analogues to Carbonic Acid Derivatives. If atoms of oxygen in the molecule of carbonic acid or its derivatives are replaced by atoms of sulphur, corresponding sulphur-containing analogues result. The most important of these are:



Solutions of sulphur in sulphur disulphide are used in what is known as the cold vulcanization of rubber.

Xanthic, or Xanthogenic, Acid. The interaction of carbon disulphide with alcohols in the presence of a caustic alkali or with alcoholates produces xanthates, salts of xanthic acid:



The xanthic acid derivatives are yellow. The free acid is very unstable and decomposes readily.

As stated earlier (p. 324), the xanthate esters of cellulose are used in the rayon industry for the production of viscose rayon. With salts of heavy metals, xanthates produce precipitates of low solubility.

The ethyl and butyl xanthates of alkaline metals are used in dressing the ores of heavy metals (Cu, Ni, Pb, Zn, etc.) by flotation. The sulphide ores of metals contain mixtures of silicate rocks (sodium, calcium, magnesium, and other silicates) and sulphides of heavy metals (lead glance PbS , copper pyrite CuS , sphalerite ZnS , etc.). To separate the sulphides from the gangue, the ore is first crushed and agitated in water. If a small amount of xanthates

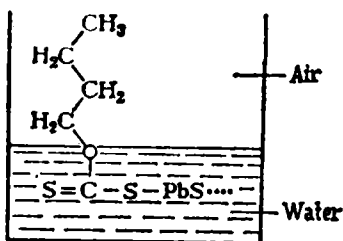


Fig. 57. Distribution of xanthate particles at water-air interface.

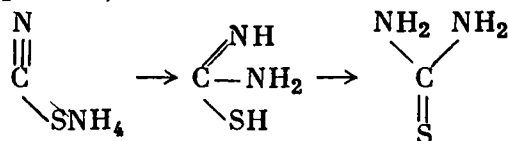
is now added to this pulp, their molecules are firmly adsorbed on the surface of the ore crystals (this being due to the xanthic group). The ore particles with the xanthate adsorbed on their surface tend to concentrate at the *water-air interface* (Fig. 57).

In the flotation machine, frothers (pine oil, turpentine oil, etc.) are added to the pulp, which is subjected to intense agitation, while air is passed through it. The air bubbles become covered with ore particles at the surface and rise to the surface of the water. The continuously revolving wooden impellers separate this froth with the ore from the suspended gangue, since silicate minerals have no affinity for xanthates and are not transferred into the froth. Flotation reagents in this way effect a paradoxical process: heavy minerals are made to "float", while the lighter silicates remain at the bottom.

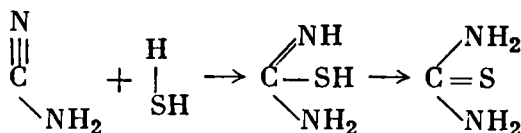
By a chemical procedure of this type small amounts of flotation reagents make it possible to achieve a high degree of concentration of even poor ores. The use of different reagents and chemical treatment renders possible the partial separation of mixtures of ores: copper-iron, lead-zinc, and others.

Thiourea NH_2CSNH_2 is in most of its properties a complete analogue to urea. It was first prepared by heating ammonium thiocyanate (similarly to the preparation of urea from ammonium cyanate,

as described on p. 377):



At present thiourea is prepared by the action of hydrogen sulphide on cyanamide:

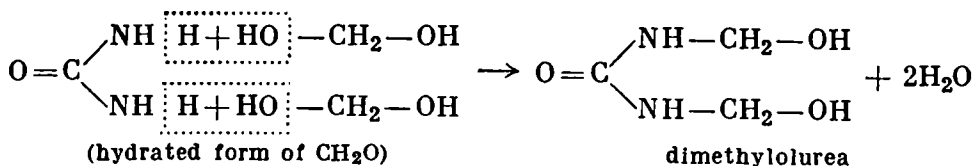


Thiourea is a crystalline substance (m.p. 180°), which is soluble in water. It is used in photography (e.g., for sepia dyeing of prints) and in the synthesis of drugs. It is interesting to note that the treatment of potato tubers with thiourea causes them to sprout without wintering.

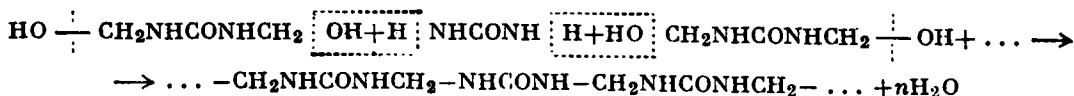
208. Plastics Based on Urea-Formaldehyde (Carbamide) Resins. The Amino Plastics. Urea, as well as its derivatives (thiourea, dicyandiamidine, etc.), condenses with formaldehyde to form resin-like products; these are carbamide resins, which serve to make what are known as *amino plastics*.

To have some idea of the structure of the complex molecules of such plastics, let us consider the formation of urea-formaldehyde condensation products schematically.

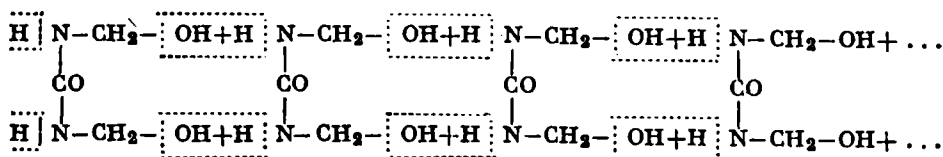
One of the first stages in this complex reaction is the formation of *dimethylolurea*:



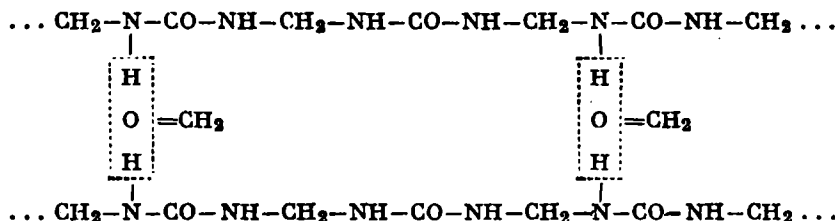
When dimethylolurea is heated with urea in the presence of acid additions (e.g., oxalic acid), a reaction of polycondensation takes place with the liberation of water:



In addition to this, the dimethylolurea molecules can also form polycondensation products with one another:



The formaldehyde molecules in the mixture can "cross-link" the linear molecules:



This gives rise to a complex mixture of linear and spatial molecules of very high weight.

Depending on the conditions in which the process is conducted, resins of different types are obtained; they find very many industrial applications.

The carbamide resins are colourless and can easily be given any colour. They are used on a large scale for gluing and impregnating timber, for decorative articles, for the manufacture of consumer goods (lamps, lamp-shades, telephones, and dishes) and lacquers. A light, porous material called *mipora* is also made from urea resins and is used for heat- and sound-insulation.

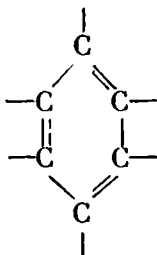
Thiourea can be used as a substitute for urea; and other aldehydes, as substitutes for formaldehyde.

Part Two

CARBOCYCLIC COMPOUNDS

COMPOUNDS OF THE AROMATIC SERIES

The compounds of the aromatic series are substances whose molecules contain the specific group of six carbon atoms referred to as the benzene nucleus, or ring,



CHAPTER XVIII

Monocyclic Aromatic Compounds

BENZENE AND ITS HOMOLOGUES

209. Properties of Benzene. The parent substance of the aromatic compounds is benzene C_6H_6 . It is a colourless, mobile liquid (relative density $d_4^{20} = 0.879$), which boils at 80.1° ; it has a characteristic odour, does not dissolve in water, ignites readily and burns with a bright smoky flame. When cooled, benzene solidifies into a white crystalline mass, which melts at 5.5° . Benzene has many industrial applications as the material for the production of a number of valuable organic substances and as a solvent. Large amounts of it are used as additions to petrol.

The story of the discovery of benzene is rather interesting. After the introduction of gas lighting in London in 1812-15, the illuminating gas, prepared from the fat of marine animals, used to be delivered to the city in iron containers. The containers were usually kept in basements, and from there the gas was piped throughout the house. But an extremely unpleasant fact was noticed rather soon: in very cold weather the gas seemed incapable of burning with

a bright flame. In 1825 the owners of the gas works consulted Michael Faraday* on the subject. He found that in these cases the gas constituents capable of burning with a bright flame condensed on the bottom of the container in a transparent liquid layer.

When investigating this liquid, Faraday discovered a new hydrocarbon: benzene.

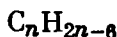
Benzene, its derivatives, and the substances of similar structure make up the division of so-called *aromatic compounds*. It will be remembered that the open-chain compounds considered earlier belong to the aliphatic division (the Greek word *aleiphar* meaning fat). Since these terms might suggest wrong notions, they require some explanation.

The earliest representatives of the group of organic acids, alcohols, ethers and esters were closely related to products obtained from fats. Much later it was established that these compounds have open chains of carbon atoms. Nevertheless, the compounds of acyclic structure came to be known as "compounds of the aliphatic division".

The first benzene derivatives were isolated from aromatic resins (benzoin gum, etc.). It was later established that the molecules of such compounds have ringed structures, similar to the structure of benzene. Compounds of this type were therefore classified as aromatic.

Distinctive Features of Aromatic Compounds. Benzene is the chief representative of the aromatic hydrocarbons. First of all, we must consider several of its specific properties, distinguishing it from the saturated and unsaturated acyclic (aliphatic or "fatty") hydrocarbons, which we examined earlier. It is common to refer to the so-called "aromatic character" of benzene, reflected in its chemical properties and due to its chemical structure.

In composition, benzene and its homologues are unsaturated hydrocarbons. The composition of benzene is expressed by the formula C_6H_6 . The general formula of the benzene series homologues is:

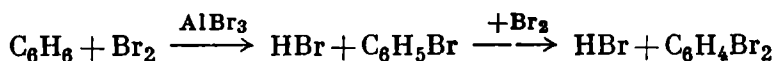


When we compare this formula with that of the saturated hydrocarbon series C_nH_{2n+2} , it becomes quite evident that the difference between them amounts to 8H. This would appear to indicate that in chemical composition benzene is a distinctly unsaturated compound. *Its unsaturated character is not, however, evident in typical*

* Michael Faraday (1791-1867), the famous English chemist and physicist, was born in London, where his father was a blacksmith. In his youth he worked as a bookbinder. He is best known as a scientist for his investigations in electricity. His work in organic chemistry included the discovery of benzene in illuminating gas, the discovery of butylene, and the preparation of α - and β -naphthalene sulphonic acids.

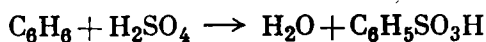
reactions. We would expect benzene to behave like ethylene, divinyl, and other typical unsaturated hydrocarbons. In reality, however, it does not make bromine water colourless, i.e., does not add bromine in ordinary conditions. Nor is a solution of potassium permanganate rendered colourless by shaking with benzene, i.e., benzene is stable in these conditions to oxidation. Even prolonged boiling with a KMnO_4 solution scarcely oxidizes benzene at all. Typical of benzene are substitution reactions. It differs in its properties from unsaturated compounds in that it enters into substitution reactions more readily than into addition reactions.

In the presence of catalysts (FeCl_3 , AlCl_3) chlorine and bromine are not added to benzene, but replace hydrogen atoms in its molecule:

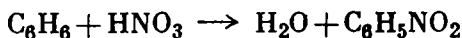


This reaction was discovered in 1877 by G. Gustavson*.

Concentrated sulphuric acid does not cause the polymerization of benzene, but produces benzenesulphonic acid:



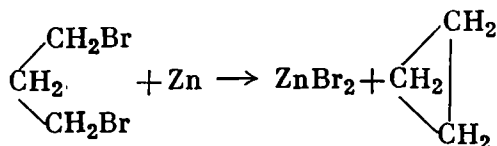
A nitration mixture (concentrated $\text{HNO}_3 + \text{H}_2\text{SO}_4$) produces nitration:



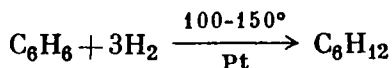
Several more substitution reactions will be mentioned later in which benzene and its derivatives behave as saturated compounds. In certain conditions, however, the unsaturated character of benzene becomes fully apparent. Various addition reactions are a case in point.

Addition Reactions of Benzene. Hydrogenation, i.e., the addition of hydrogen, takes place under the action of gaseous hydrogen in the presence of certain metals (Ni, Pt, Pd) in powdered form. The

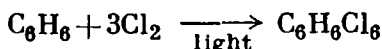
* Gavriil Gustavson (1842-1908) was an outstanding Russian chemist. His early work was done under the direction of D. Mendeleev and was concerned with the exchange reactions of anhydrous salts of metals. He discovered the catalytic effect of the aluminium halides on certain reactions of aromatic compounds. This discovery was later applied by Friedel and Crafts in France to the well-known reaction of the alkylation of aromatic compounds. The mechanism of this reaction had been studied thoroughly by Gustavson. He also discovered the general reaction of the synthesis of cyclopropane hydrocarbons by removing two bromine atoms from dibromides by means of zinc:



benzene molecule in this case adds three molecules of hydrogen:

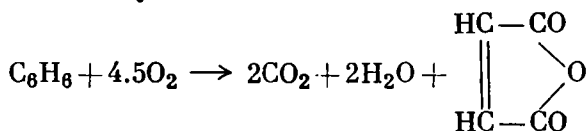


If a solution of chlorine or bromine in benzene is subjected to the action of light rich in violet and ultraviolet rays (direct sunlight or a quartz lamp), there is likewise rapid addition of three halogen molecules:



Addition reactions thus point to the presence of three double bonds in benzene.

Oxidation Reactions of Benzene. If benzene vapours are led with oxygen at an elevated temperature (400°) over certain catalysts (V_2O_5), the benzene is oxidized with the formation of carbon dioxide and maleic anhydride:



A benzene molecule adds three molecules of ozone. Hence, in this reaction too benzene behaves as if its molecule had three double bonds.

The aromatic character of benzene may thus be summarized as follows: the compound is unsaturated in composition, but in a number of chemical reactions behaves as a saturated compound; it is marked by chemical stability and enters into addition reactions with difficulty; in certain specific conditions (catalysts, irradiation) it acts as if its molecule had three double bonds. These specific properties of benzene may be traced to the chemical structure of its molecule.

210. Structure of Benzene. The substitution of a bromine atom for one hydrogen atom in the benzene molecule yields only monobromobenzene $\text{C}_6\text{H}_5\text{Br}$. Similarly, we know of only one monochlorobenzene. This is a general rule: *the monosubstituted benzenes have no isomers*. Hence, all the hydrogen atoms in benzene are equivalent, and it makes no difference which of them is replaced.

On the other hand, the products of the replacement of two hydrogen atoms in the benzene molecule—the disubstituted derivatives of benzene—are known in the form of three isomers, designated by the prefixes ortho, meta, and para (or their abbreviations *o*-, *m*-, and *p*- respectively). There are thus three dibromobenzenes $\text{C}_6\text{H}_4\text{Br}_2$: *o*-dibromobenzene (m.p. 6.7°), *m*-dibromobenzene (m.p. -7°), and *p*-dibromobenzene (m.p. 87°).

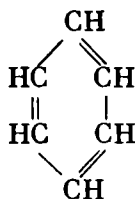
The structural formula of benzene should therefore account for the following facts:

1) why the benzene molecule can add only six atoms of a halogen or hydrogen;

2) why there are no isomers of the monosubstitution products of benzene, and

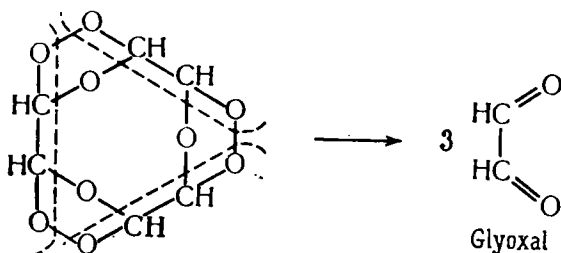
3) why the disubstitution products are known in the form of three isomers.

The structure of benzene is in most cases expressed by the formula proposed by Kekulé * in 1865:



According to this formula, the six carbon atoms in the benzene molecule form a closed carbon chain, the so-called benzene ring; hence, the benzene molecule can add six atoms of hydrogen or a halogen. At the same time the formula shows that there are three double bonds between the carbon atoms in the benzene molecule.

In complete conformity with this is the formation of glyoxal when the triozone of benzene is decomposed by water:

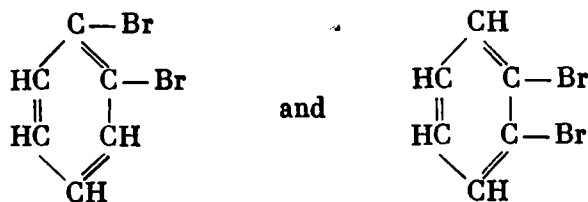


The benzene formula advanced by Kekulé accounted for many other experimental facts; some facts, however, could not be inter-

* Friedrich August Kekulé (1829-96) was born in Darmstadt. A pupil of Liebig's, he became a professor of chemistry first at the University of Ghent and then at the University of Bonn. His main contributions were to theoretical chemistry. In 1854 he was the first to suggest the idea of the "dibasicity", i.e., the divalency, of oxygen and sulphur. Carbon was regarded by him as a tetravalent element. Kekulé advanced the theory of polyatomic radicals, thereby extending the scope of Gerhardt's theory of types. In 1865 he suggested the cyclic formula of the structure of benzene with alternate single and double bonds.

Kekulé prepared thioacetic acid; in 1856 he devised the method of preparing glycolic acid by boiling chloroacetic acid with water; in 1872 he prepared triphenylmethane and anthraquinone.

preted easily on its basis. For example, according to Kekulé's formula, there should be two series of isomeric disubstituted benzene derivatives:



In the former formula the two bromine atoms are attached to doubly bound carbon atoms, whereas in the latter formula they

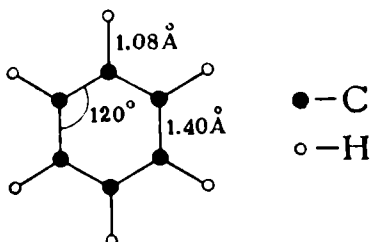
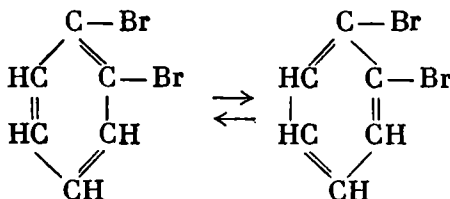


Fig. 58. Structure of the benzene molecule.

are attached to singly bound carbon atoms. Since no such isomerism had ever been observed in benzene derivatives, Kekulé put forward the hypothesis that the single and double bonds in the benzene molecule were not in fixed positions, but could oscillate between two positions:



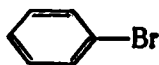
This came to be known as the *oscillatory hypothesis*.

So simple and so convenient in practice is Kekulé's formula that chemists continue to use it to this day, although neither the basic assumption that single and double bonds in the benzene ring alternate nor the oscillatory hypothesis has been borne out by modern science.

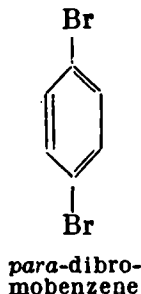
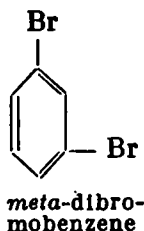
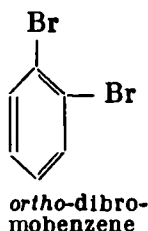
Present-Day Notions Concerning the Structure of Benzene. By means of modern physical techniques it has been established that the benzene molecule has the following structure (Fig. 58).

1. The carbon atoms form a regular plane hexagon with sides equal to 1.40 Ångström units. Consequently, the length of the C—C linkage in benzene is less than the C—C single-bond distance (1.54

equivalent. Therefore the replacement of any one of them, say, by a bromine atom, yields the same bromobenzene:



But if a second bromine atom is introduced into bromobenzene, three different substances can be formed:



As is evident from these formulas, the isomerism of the resulting compounds is due to the different position of the bromine atoms in relation to each other.

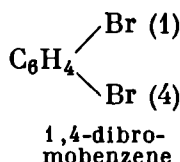
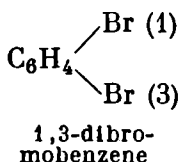
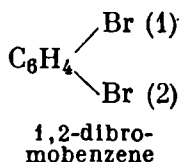
If the hydrogen atoms of two adjacent carbon atoms are replaced, the resulting compounds are called *ortho-isomers*.

If the hydrogen atoms replaced are attached to carbon atoms separated from each other by one carbon atom, the resulting compounds are called *meta-isomers*.

Finally, if the substituents are attached to carbon atoms separated from each other by two carbon atoms, the resulting compounds are called *para-isomers*.

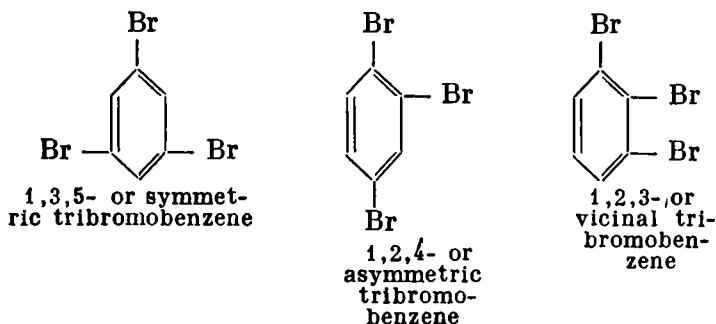
To indicate the position of a substituent the carbon atoms of the benzene ring are numbered, one of the atoms where substitution has taken place being designated as No. 1.

The formulas of the dibromobenzene isomers can also be written as follows:



When three hydrogen atoms in the benzene molecule are replaced by *identical* atoms or groups, the following isomers are pos-

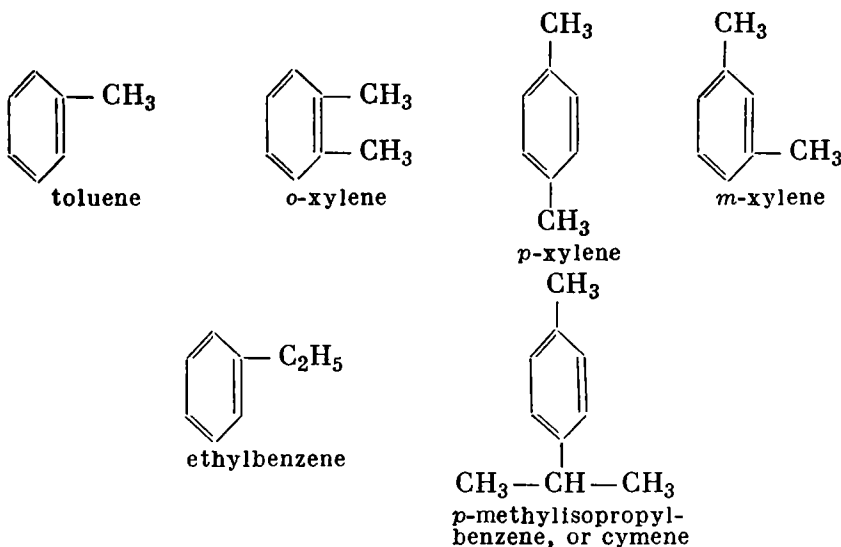
sible:



Three isomers are also possible for the tetra-substituted derivatives of benzene (with identical substituents), but there is no isomerism among the penta- and hexa-substituted derivatives.

By consecutively replacing from one to six hydrogen atoms in the benzene molecule by chlorine, it is thus possible to obtain twelve chlorine substitution products of benzene. They were prepared in the years 1875 to 1880 by F. Beilstein and A. Kurbatov.

212. Structure and Properties of Benzene Homologues. The substitution of alkyls for hydrogen atoms in the benzene molecule gives rise to a series of benzene homologues exemplified by



The benzene hydrocarbons are colourless liquids, which are lighter than water and cause very considerable refraction of a ray of light; they have a characteristic odour and do not dissolve in water (Table 15).

The benzene hydrocarbons have higher relative densities and refractive indices than the saturated hydrocarbons, e.g.:

C_6H_6	$d_4^{20} = 0.879$	$n_D^{20} = 1.5017$
C_6H_{14}	$d_4^{20} = 0.681$	$n_D^{20} = 1.3754$

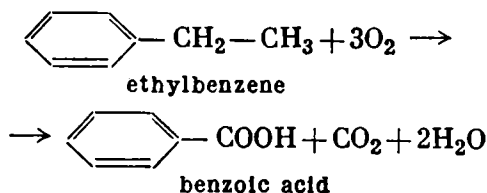
TABLE 15. Physical Properties of Benzene Homologues

Homologue	Formula	M.p., °C	B.p., °C
Benzene	C_6H_6	5.5	80.1
Toluene	$C_6H_5CH_3$	-95.1	110.6
<i>o</i> -Xylene	$C_6H_4(CH_3)_2$	-25.2	144.4
<i>m</i> -Xylene	$C_6H_4(CH_3)_2$	-47.9	139
<i>p</i> -Xylene	$C_6H_4(CH_3)_2$	13.2	138.4
Ethylbenzene	$C_6H_5C_2H_5$	-95.0	137
Cymene	$C_6H_4(CH_3)-CH(CH_3)_2$	-67.2	177

The groups of atoms obtained from the benzene hydrocarbons by the removal of one hydrogen atom (from among the atoms attached directly to the benzene ring) are called aromatic radicals, or *aryls*. The benzene radical C_6H_5 is called *phenyl*; the toluene radical $CH_3C_6H_4$, *tolyl*, and the xylene radical $(CH_3)_2C_6H_3$, *xylyl*. The divalent radical C_6H_4 is called *phenylene*.

A consideration of the structural formulas of the benzene hydrocarbons makes it evident that in the molecules of these substances we must distinguish, on the one hand, the benzene nucleus (or ring) and, on the other, the aliphatic hydrocarbon radical linked to it as a side chain. In toluene, for example, the side chain consists of a methyl radical; in ethylbenzene, of an ethyl radical, and in cymene there are two side chains consisting of a methyl and an isopropyl radical respectively. Such hydrocarbons are called *fatty aromatic*.

In the compounds of the fatty aromatic series the benzene ring retains the specific feature of benzene. For example, it exhibits a high stability towards oxidizing agents. When fatty aromatic hydrocarbons are treated with strong oxidants (e.g., potassium permanganate), the side chain undergoes oxidation, the carbon atom closest to the ring remaining attached to the ring and forming a carboxyl:



It should be noted that in diamond crystals, as well as in compounds of the fatty series, the carbon atom valencies are directed towards the vortices of a tetrahedron (p. 152), while in graphite (Fig. 59)

the carbon atoms are situated in parallel planes, the atoms in each plane being in the vortices of regular hexagons.

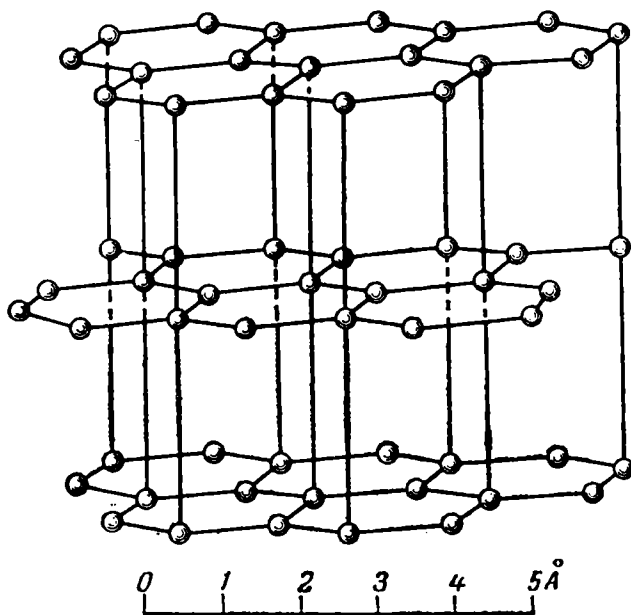
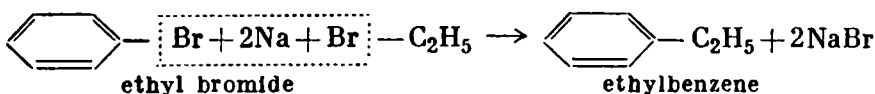


Fig. 59. Graphite crystal lattice.

213. Preparation of Benzene Homologues. 1. *The Fittig synthesis* is effected by the action of sodium on a mixture of bromobenzene and a halogen derivative of a saturated hydrocarbon:

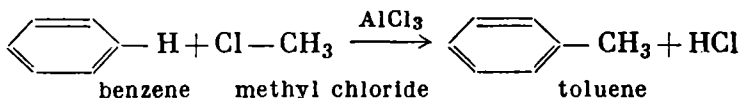


To prepare ethylbenzene 27 g of thinly sliced sodium are placed in a flask with a reflux condenser (Fig. 60) and 200 ml of thoroughly dried ether are added. In a few hours, when the sodium has dried the ether completely, 60 g of ethyl bromide and 60 g of bromobenzene are poured into the flask through the reflux condenser. The mixture is then left overnight. If it begins to boil, the flask is cooled by water. First the ether and then the ethylbenzene are distilled off the following day. The preparation of some hydrocarbons by this reaction calls for the heating of the mixture on a water bath or an oil bath.

It is evident from the above equation that the Fittig synthesis is quite similar to the Wurtz synthesis of saturated hydrocarbons (p. 52). The synthesis served to establish the structure of toluene, ethylbenzene, xylene, and a number of other aromatic compounds.

2. *The Friedel-Crafts Synthesis.* When a mixture of benzene and an alkyl chloride is heated in the presence of anhydrous aluminium chloride, a hydrogen atom in the benzene molecule is replaced by

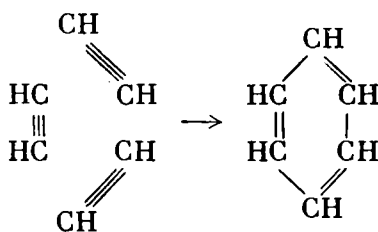
the alkyl with the evolution of hydrogen chloride:



This reaction was discovered in 1877 by the French chemist Friedel and his American co-worker Crafts. Their investigations were suggested by the work of the Russian chemist Gustavson.

3. *The Reduction of Aromatic Ketones* (p. 431).

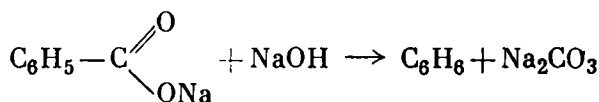
4. *The Polymerization of Unsaturated Compounds of the Fatty Series.* Benzene, as well as some of the benzene hydrocarbons, can be prepared from compounds of the fatty series. For instance, the heating of acetylene to 550-600°, as shown by Berthelot in 1866, converts it to benzene:



What takes place is the rupture of one of the bonds in the C≡C group in the acetylene molecules; the valencies of one acetylene molecule thus made free are then saturated by the freed valencies of another molecule. Three acetylene molecules in this way form one benzene molecule.

N. Zelinsky and B. Kazansky showed that this reaction proceeds very well when acetylene is passed through activated charcoal heated to 600-650°.

5. *Synthesis from Salts of Aromatic Acids.* When dry salts of aromatic acids are heated with sodium hydroxide, the salts decompose with the formation of hydrocarbons:



This method is analogous to one of the methods of preparing hydrocarbons of the fatty series.

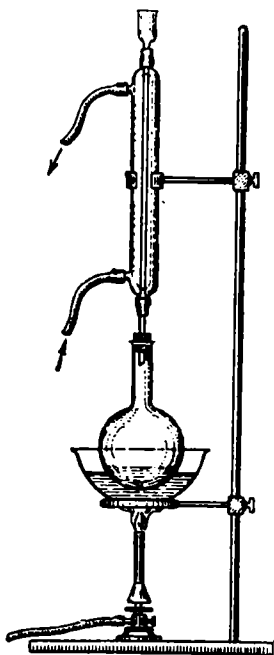


Fig. 60. Laboratory installation for preparing benzene homologues.

214. Industrial Manufacture of Aromatic Compounds. The principal sources of benzene and other aromatic hydrocarbons up to the middle of the 20th century were coal-tar and coke-oven gas, produced by the destructive distillation of coal. With the rapid expansion of the chemical industry and the parallel growth of the petroleum-refining industry in recent years, greater and greater quantities of aromatic hydrocarbons have been obtained from petroleum products.

Coal is subjected to destructive distillation at coking and chemical plants to obtain metallurgical coke. The process yields coke-oven gas, coal-tar, ammonia water, and coke. The coal-tar produced accounts for 3-6% of the mass of the coal. It contains a large number of various aromatic hydrocarbons.

The content of benzene in coal-tar is low (0.05-0.1%). The bulk of the benzene is extracted from the coke-oven gas through absorption by high-boiling coal-tar cuts (heavy oil). Raw coke-oven gas contains 25-35 g/cu m of a mixture of aromatic hydrocarbons of approximately the following composition: 70-80% benzene, 16-20% toluene, 5% xylenes, and 2% other compounds. The coke-oven gas produced by the destructive distillation is passed through several cooling installations to separate the coal-tar. Following this, it is passed through scrubbers, where it is washed with water, which absorbs the ammonia in the gas. Rid of coal-tar and ammonia, the gas goes on to absorber washers for the aromatic hydrocarbons to be extracted. The absorbed aromatic hydrocarbons are separated from the absorbent oil by distillation. After this the aromatic hydrocarbons are purified by sulphuric acid or by hydrogenation under pressure (to rid them of sulphide and unsaturated compounds). The individual hydrocarbons are isolated from the crude benzole by distillation.

The coal-tar is usually divided by distillation into the following cuts:

(1) *light oil*, which boils below 170° and contains benzene and its homologues (this cut does not exceed 3% of the mass of the coal-tar);

(2) *middle*, or carbolic, *oil*, which boils in the 170-230° range and contains phenol, naphthalene, and pyridine bases;

(3) *heavy*, or creosote, *oil*, which boils in the 230-270° range and contains cresols, xylenols, quinoline, polycyclic hydrocarbons, and some phenol, naphthalene, and anthracene, and

(4) *anthracene oil*, which boils in the 270-340° range and is often vacuum-distilled to reduce the boiling point. It contains anthracene, phenanthrene, carbazole, and polycyclic hydrocarbons.

The residue after coal-tar distillation is a thick mass called *pitch*, which is used to make varnishes, road surfaces, and to impregnate timber (for example, railway ties).

The individual compounds are extracted from coal-tar cuts by a combination of rectification and crystallization methods. The total yield of aromatic hydrocarbons in destructive distillation amounts to approximately 1% of the original coal.

The coking and chemical industry has already proved unable to meet the demand for aromatic hydrocarbons in the rapidly expanding production of synthetic materials. Moreover, the use of petroleum hydrocarbons makes possible more highly directional industrial processes for producing the desired compounds than in the case of the destructive distillation of coal.

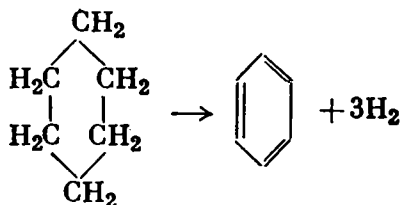
Aromatic hydrocarbons can be produced from petroleum or from individual petroleum cuts by pyrolysis, i.e., by heating to high temperatures (700° and higher). Petroleum pyrolysis is today practised on a big scale for the commercial production of ethylene and propylene. The liquid by-products of the process serve for the additional production of aromatic hydrocarbons. Certain quantities of benzene and its homologues are also produced in the catalytic cracking process.

The principal technique for obtaining aromatic hydrocarbons from petroleum products is the catalytic process, first developed by N. Zelinsky, B. Kazansky, and other Soviet scientists.

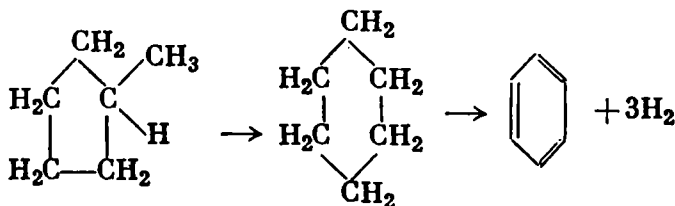
The process is conducted over different catalysts and under different conditions according to the initial petroleum material and desired products. The most frequently used catalyst is platinum deposited on alumina, which has given the process the name *plating*. Usually it is conducted at a temperature of about 500° and a pressure of 20-30 atm.

The naphthene and paraffin hydrocarbons contained in the initial petroleum undergo complex chemical changes in the process, with the formation of aromatic hydrocarbons.

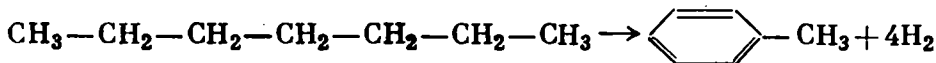
The naphthene hydrocarbons either experience dehydrogenation



or else are dehydrogenated with simultaneous ring expansion



The paraffin hydrocarbons undergo dehydrocyclization (i.e., the loss of hydrogen with simultaneous ring-closure):



Usually aromatic hydrocarbons account for up to 50% of the reaction products. They are separated from the paraffin and other hydrocarbons by extraction with solvents and are then purified by rectification.

The catalytic aromatization of petroleum products was first effected on an industrial scale to improve the quality of petrol and soon became very widespread. The effect of the process on the quality of motor fuel can be seen from the following example. The octane number of toluene is 120, i.e., it is nearly three times higher than the octane number of 2-methylhexane, which contains the same number of carbon atoms in the molecule and has the octane number 43.

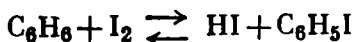
At present the processes of catalytic aromatization are also used extensively to produce benzene and other aromatic hydrocarbons.

HALOGEN DERIVATIVES OF BENZENE AND OF ITS HOMOLOGUES

215. Preparation of Halogen Derivatives of Benzene Hydrocarbons. The chlorine and bromine derivatives of the benzene hydrocarbons are usually prepared by the direct action of chlorine or bromine on the hydrocarbons. Benzene in the presence of catalysts reacts readily with chlorine or bromine. By selecting suitable reaction conditions and catalysts, it is possible to substitute the halogen consecutively for all the hydrogen atoms linked to the benzene ring.

Fig. 61 shows a set-up for the laboratory preparation of bromobenzene. For the reaction to take place, some large iron filings are placed in the flask. The benzene is then poured into the flask and the bromine added with stirring. A small amount of bromine is added at first; the flow of bromine is increased when the evolution of hydrogen bromide begins. The rate at which the bromine is introduced should not be too great, lest the reaction should proceed too violently. The ferric bromide FeBr_3 formed serves as the catalyst in this reaction.

The direct introduction of iodine into aromatic compounds is fraught with great difficulties, since the hydrogen iodide formed in the reaction partly reduces the iodobenzene to the initial substance:



For the direct preparation of iodobenzene, a mixture of benzene, iodine, and iodic acid is heated in a sealed tube. The iodic acid oxidizes the hydrogen iodide to free iodine.

The homologues of benzene undergo chlorination and bromination more readily than benzene does. The halogen in this case can

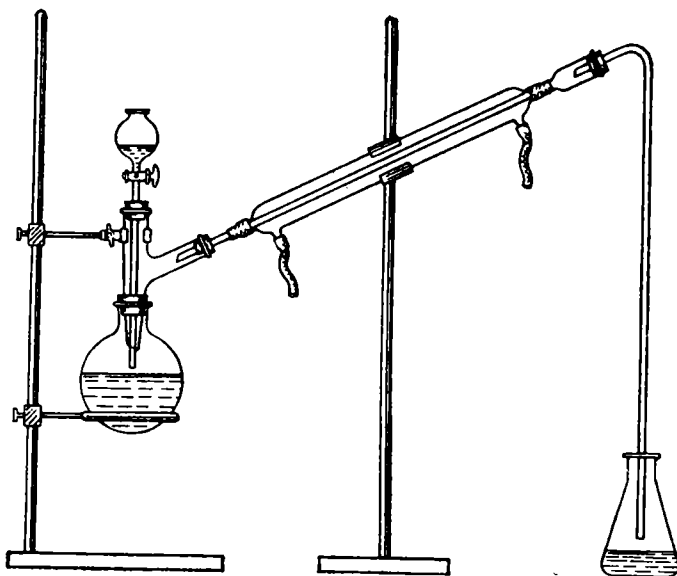
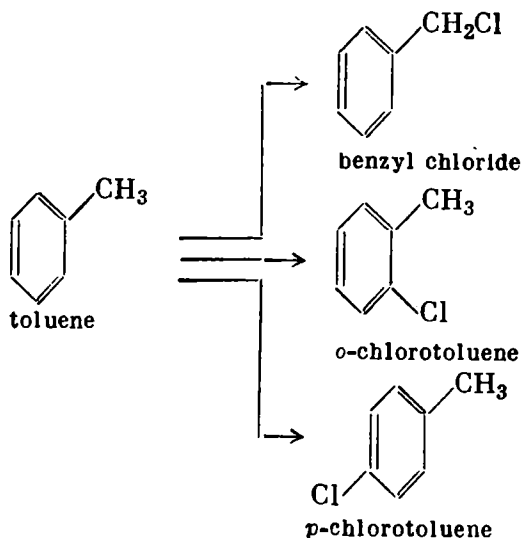


Fig. 61. Set-up for preparing bromobenzene.

either enter the side chain or replace a hydrogen atom of the benzene ring. For instance, the introduction of chlorine into the side chain of toluene yields *benzyl chloride* $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, named so according to the benzyl radical $\text{C}_6\text{H}_5\text{CH}_2-$.

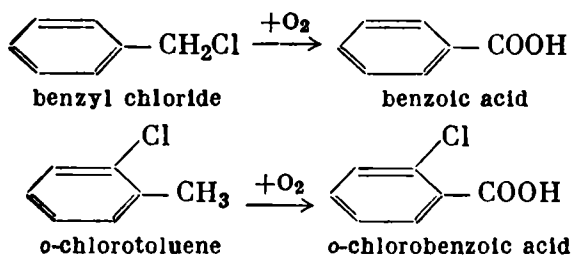
The substitution of chlorine for a hydrogen atom attached to the ring yields *chlorotoluene* (a mixture of ortho- and para-isomers):



As demonstrated by Beilstein as early as 1886, the chlorination of toluene at a low temperature in the presence of a catalyst (I_2) causes substitution in the ring, whereas at higher temperatures the chlorine goes into the side chain.

When the hydrocarbon is treated with a halogen in direct sunlight, side-chain substitution products exclusively are formed.

The position of the halogen can be determined by oxidizing the substance. For example, benzyl chloride upon oxidation yields benzoic acid, while chlorotoluene yields chlorobenzoic acid:



216. Properties of Halogen Derivatives of Benzene Hydrocarbons. The halogen derivatives of the benzene hydrocarbons are either liquids or solids (Table 16).

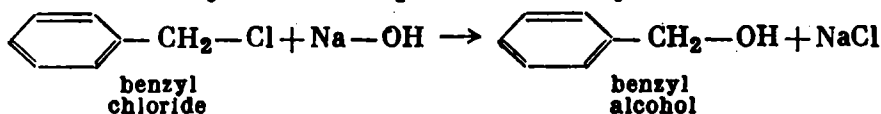
Substances in which the halogen is attached to the carbon atom of the side chain have a pungent, irritating odour. Some of them, such as *benzyl bromide* $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, were used in the First World War as lachrymatory chemical warfare agents.

The halogen attached to the α -carbon atom of the side chain is highly mobile and can easily be replaced by a hydroxyl, cyan, etc., in other words, it behaves in the same way as in halogen derivatives of the fatty series. For instance, the action of sodium

TABLE 16. Physical Properties of Some of the Halogen Derivatives of Benzene Hydrocarbons

Derivative	Formula	M.p., °C	B.p., °C
Chlorobenzene . . .	$\text{C}_6\text{H}_5\text{Cl}$	-45	132
Bromobenzene . . .	$\text{C}_6\text{H}_5\text{Br}$	-30.6	156.2
Iodobenzene	$\text{C}_6\text{H}_5\text{I}$	-31.4	188.7
Benzyl chloride . .	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	-39	179
Benzyl bromide . .	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	-3.9	198
Benzylidene chloride	$\text{C}_6\text{H}_5\text{CHCl}_2$	-17.4	205.3
Benzotrichloride . .	$\text{C}_6\text{H}_5\text{CCl}_3$	-4.8	220
o-Chlorotoluene . . .	$\text{C}_6\text{H}_4(\text{CH}_3)\text{Cl}$	-36.5	159.2
Hexachlorobenzene	C_6Cl_6	229	322

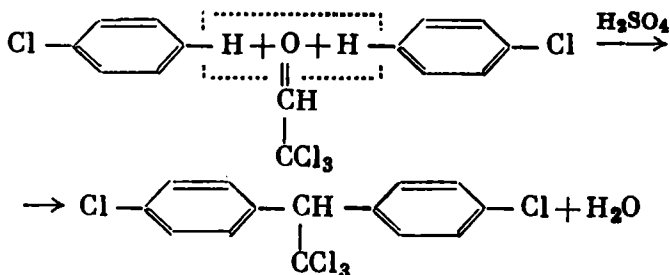
hydroxide on benzyl chloride produces benzyl alcohol:



Compounds containing a halogen in the ring have a faint pleasant odour. The halogen in these compounds is linked to the ring quite strongly. It is not mobile and can be replaced only in special conditions. In the chlorobenzene molecule, for instance, the chlorine can be replaced by a hydroxyl only by heating the chlorobenzene with an alkali solution to 300-350° usually in the presence of copper. In this respect substances containing a halogen attached directly to a carbon atom of the ring are like the halogen derivatives of unsaturated hydrocarbons with the halogen attached to a doubly bound carbon atom; the halogen in such compounds likewise exhibits little mobility.

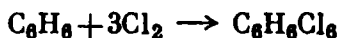
217. Some Representative Halogen Derivatives of Benzene Hydrocarbons. *Chlorobenzene* is a liquid boiling at 132°; it is prepared in large quantities and used as an intermediate product in the synthesis of many organic substances, e.g., phenol and dinitrochlorobenzene, a semi-product utilized in synthesizing the dye sulphur black.

Another insecticide is DDT, or *p,p'*-dichlorodiphenyltrichloromethylmethane. It is prepared by the condensation of chlorobenzene with chloral in the presence of concentrated, or fuming, sulphuric acid:



The substance forms white crystals.

Another extremely potent insecticide is hexachlorocyclohexane $\text{C}_6\text{H}_6\text{Cl}_6$ ("hexachloran" or benzene hexachloride). This is prepared by adding chlorine to benzene in sunlight or under mercury arc lamp illumination:



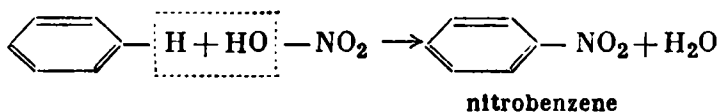
NITROGEN COMPOUNDS AND SULPHONIC ACIDS

218. Nitration. It is characteristic of aromatic compounds that when treated with nitric acid they readily form nitrogen compounds.

Whereas the saturated hydrocarbons undergo nitration with difficulty, the aromatic hydrocarbons are easily nitrated by concen-

trated nitric acid or, more often, by a mixture of concentrated nitric and sulphuric acids. The latter serves to bind the water formed in the reaction.

The reaction between benzene and nitric acid may be expressed by the following equation:

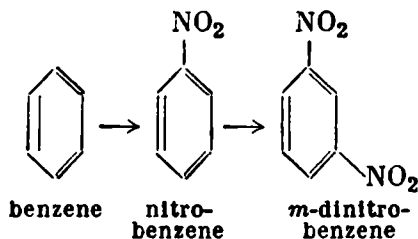


It is evident from this equation that the benzene ring loses a hydrogen atom, while the nitric acid molecule loses an OH group. The reaction product is nitrobenzene, in which a nitrogen atom is attached to a carbon atom of the benzene ring. The reaction was discovered by Mitscherlich in 1834.

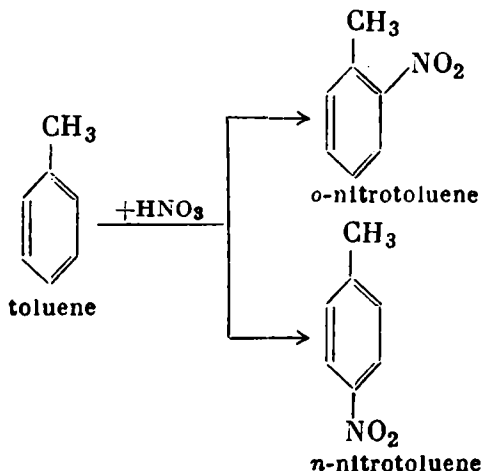
Other aromatic compounds—hydrocarbons, phenols, acids, etc.—are nitrated similarly.

Under certain conditions it is possible to introduce two and even three nitro groups into the benzene ring.

The reaction proceeds consecutively: the first product is nitrobenzene, which is then converted into dinitrobenzene:

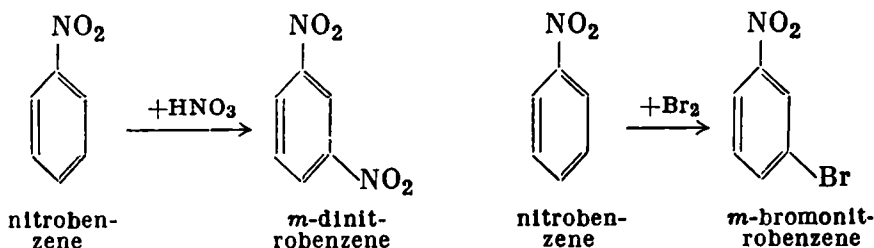


219. Directing Effect of Substituents. The nitration of toluene yields *o*- and *p*-nitrotoluenes:



As for nitrobenzene, its nitration yields *m*-dinitrobenzene almost exclusively, while its bromination yields *m*-bromonitro-

benzene:

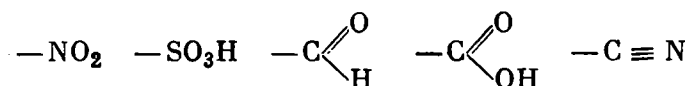


These examples show that the nature of the first substituent group influences the position which a second entering group takes up in relation to the first: groups already attached to the ring direct (or orient) a subsequent substituent.

There are two types of substituents. *The substituents of the first class have an ortho- and para-directing influence on a second group, both of these isomers usually being formed. The meta-isomer in this case is either not formed at all or is formed in a very minute quantity. Substituents of the second class cause meta-orientation of a second substituent exclusively or almost exclusively.*

The following groups, listed in order of decreasing directing effect, are substituents of the first class: $-\text{OH}$, $-\text{NH}_2$, Cl , Br , I , $-\text{CH}_3$, and other alkyls.

The substituents of the second class include the groups:

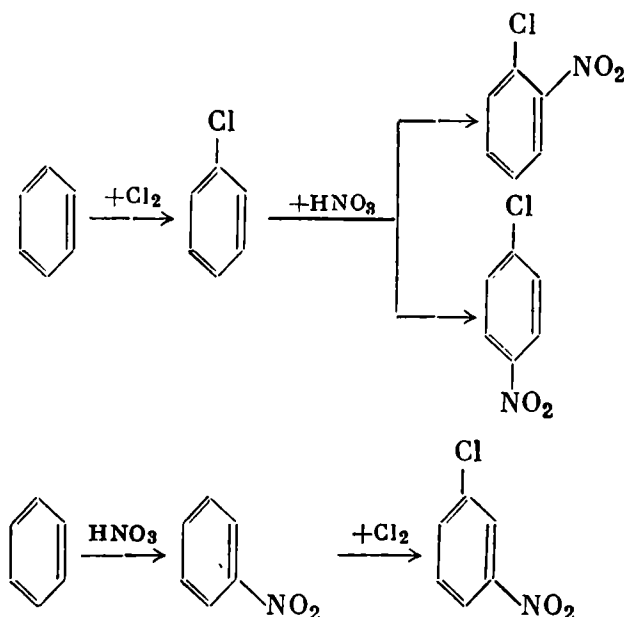


Many second-class substituents have double or triple bonds.

The formation of different quantities of ortho-, meta-, and para-isomers is due to the fact that the three competing reactions of ortho-, meta-, and para-substitution proceed simultaneously, but at different rates.

The rules of substitution in the benzene ring are very important, since an understanding of them makes it possible to predict the course of a reaction and choose the correct procedure for synthesizing this or that required substance. The orienting effect of substituents is illustrated by the formation of various isomers of nitrochlorobenzene. A nitrogen derivative of chlorobenzene can be prepared either by first chlorinating benzene and then nitrating the chlorobenzene formed or by first nitrating the benzene and then chlorinating the nitrobenzene formed. Chlorine is a substituent of the first class, and the nitration of chlorobenzene therefore yields *o*- and *p*-nitrochlorobenzenes. The nitro group, on the other hand, is a second-class substituent, and the chlorination of nitrobenzene therefore yields *m*-nitrochlorobenzene. By thus altering the order of the reaction it is possible to obtain all three isomers of nitrochloro-

benzene:



Substituent groups not only have an orienting effect on a second substituent, but also influence the mobility of the hydrogen atoms attached to the benzene ring. Second-class substituents reduce the mobility of these atoms, whereas first-class substituents enhance it. Accordingly, benzene homologues, like toluene and xylene, undergo nitration more readily than benzene itself does.

The Orientation Rules from the Standpoint of Electronic Concepts. As pointed out earlier (p. 393), the electron clouds of the π -bonds are highly mobile; for this reason it is only in non-substituted benzene C_6H_6 that all the atoms have the same electron density. The entry of substituents (e.g., Cl, OH, and NO_2) causes a considerable redistribution of the electron density in accordance with the nature of the substituents.

Let us introduce the following designations for the atoms of the substituent group:

A for the atom attached directly to the benzene ring, and B_n for the other atoms* of the substituent group.

In substituents of the first class ($\bar{A}$) ($\bar{B}_n$) ($-\text{OH}$, $-\text{NH}_2$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{CH}_3$) the A atom, linked to the benzene ring, is as a rule more distinctly electronegative than the B_n atom or group of atoms.

The free (unshared) electron pairs of the A atoms increase the electron density of the benzene ring primarily in ortho- and para-positions. The curved arrows in Fig. 62 show the direction of the

* In the case of monoatomic substituents $B_n = 0$.

electron displacement and the carbon atoms of the ring which acquire an increased electron density.

In substituents of the second class ($\overset{+}{A}$) ($\bar{B}_n$) ($-\text{CO}_2\text{H}$, $-\text{SO}_3\text{H}$, $-\text{NO}_2$) the A atom, linked to the benzene ring, is as a rule more distinctly electropositive than the B_n atom or group of atoms. Substituents of the second class,

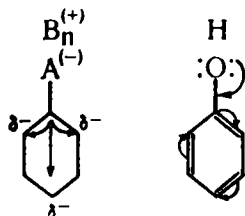


Fig. 62. Distribution of electron densities in the benzene molecule in the presence of substituents of the first class.

by attracting electron clouds, reduce the electron density in the benzene ring, especially in ortho- and para-positions (Fig. 63). The electron density at the atoms in meta-position is therefore relatively higher than in ortho- and para-positions. The most important reactions of substitution in the aromatic division, such as halogenation, nitration, sulphonation, and the Friedel-Crafts reaction, are reactions of so-called electrophilic substitution, i.e., the entering groups* $[\overset{+}{\text{Cl}}(\bar{\text{Cl}})$; $\overset{+}{\text{NO}_2}(\bar{\text{O}}\text{H})$; $\overset{+}{\text{SO}_3\text{H}}(\bar{\text{O}}\text{H})$;

$\text{CH}_3\overset{+}{\text{C}}\text{O}(\bar{\text{Cl}})]$ are electropositive and are directed primarily towards atoms that have an increased electron density. Substituents of the first class, as shown in Fig. 62, create an increased electron density in ortho- and para-positions; substituents of the second class, on the other hand (Fig. 63), do so in meta-positions. From this follow the orientation rules for electrophilic substituents.

1. *The site of entry of a substituent is determined by the orienting atom or group in the ring and does not depend on the nature of the entering substituent* (since as electrophilic substituents they all carry positive charges).

2. *Orienting atoms and groups of the first class, by increasing the electron density of the benzene ring, enhance its reactivity and have an ortho-para-directing influence upon substituents.* Toluene, phenol, and aniline do indeed undergo sulphonation, nitration, and halogenation more readily than benzene itself does, the reactions yielding primarily ortho- and para-isomers.

3. *Orienting atoms and groups of the second class, by drawing the electron clouds of benzene towards themselves, reduce the reactivity of the benzene ring; they have a primarily meta-directing influence upon substituent groups.* Such derivatives of benzene

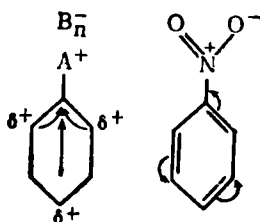


Fig. 63. Distribution of electron densities in the benzene molecule in the presence of substituents of the second class.

* The part of the molecule in the parenthesis is that which breaks away in substitution reactions.

as nitrobenzene, benzene sulphonic acid, and benzoic acid are more stable to chemical influences than benzene itself (let alone phenol, aniline, etc.); reactions with electrophilic substituents yield primarily meta-isomers. These rules are not, however, absolute. Most reactions, while yielding primarily the main product or products (in accordance with the rules), also yield other isomers, but in much smaller quantities. The principal isomers can therefore be isolated from the reaction mixture in pure form. The orienting effect of substituents is evident from Table 17.

TABLE 17. Orienting Effect of Substituents *

Substituent present in position 1	Position of entering substituent			
	Cl	Br	SO ₃ H	NO ₂
OH	4, 2	4, 2	2, 4, (3)	2, 4
NH ₂	4, (2)	—	2, 4	4, (3), (2)
CH ₃	4, 2	4, 2	4, 2, (3)	2, 4, (3)
SO ₃ H	—	3	3, (4)	3, (2), (4)
NO ₂	3	3	3, (2), (4)	3, (2), (4)
COOH	3, 2, (4)	3	3, (4)	3, 2, (4)

* The figures in parentheses denote isomers that are formed in very small quantities.

The proportion in which the isomers are obtained depends largely on the conditions in which the reaction is conducted (temperature, concentration of the reagents in the reaction mixture, etc.).

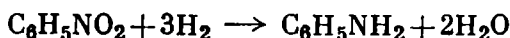
220. Properties of Nitrogen Compounds. The nitrogen compounds of the aromatic division are in most cases crystalline substances of a yellow colour. Some of their characteristics are listed in Table 18.

TABLE 18. Physical Properties of Aromatic Nitrogen Compounds

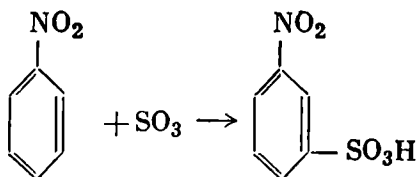
Compound	Formula	Melting point, °C	Boiling point, °C
Nitrobenzene	C ₆ H ₅ NO ₂	5.7	210.9
<i>m</i> -Dinitrobenzene . .	C ₆ H ₄ (NO ₂) ₂	89.6	302
<i>o</i> -Nitrotoluene . . .	CH ₃ C ₆ H ₄ NO ₂	−3.2	222.3
<i>p</i> -Nitrotoluene . . .	CH ₃ C ₆ H ₄ NO ₂	51.6	238
<i>m</i> -Nitrotoluene . . .	CH ₃ C ₆ H ₄ NO ₂	15.5	232.6
2,4-Dinitrotoluene . .	CH ₃ C ₆ H ₃ (NO ₂) ₂	69.6	300
2,4,6-Trinitrotoluene	CH ₃ C ₆ H ₂ (NO ₂) ₃	80.1	—

The following are some of the basic chemical properties of nitrogen compounds.

1. Nitrogen compounds are reduced to primary amines:



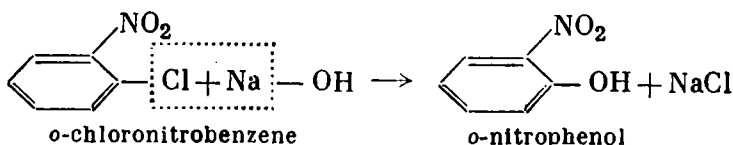
2. Replacement of the hydrogen atom in molecules of nitrogen compounds takes place in meta-position with relation to the nitro group. For instance, when nitrobenzene is treated with fuming sulphuric acid, the product is *m*-nitrobenzene sulphonic acid:



But these reactions with nitrogen compounds proceed with much greater difficulty than with hydrocarbons—the *nitro group diminishes the mobility of the hydrogen atoms of the benzene ring*. Nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$ is formed when benzene is shaken with a mixture of nitric and sulphuric acids. But the preparation of dinitrobenzene $\text{C}_6\text{H}_4(\text{NO}_2)_2$ requires heating with fuming nitric acid. The introduction of a third nitro group into the benzene molecule is accomplished with very great difficulty.

Fig. 64. Nitrator (cross-section).

3. A halogen connected to a carbon atom of the benzene ring has little mobility; its replacement is very difficult to achieve. If, however, a nitro group is introduced in ortho- or para-position with relation to the halogen, the latter acquires considerable mobility. (This was first noted by A. Engelhardt and P. Lachinov in 1870.) Accordingly, in *o*- and *p*-nitrochlorobenzenes a hydroxyl can be substituted for the chlorine by heating to 100° with a solution of sodium hydroxide:



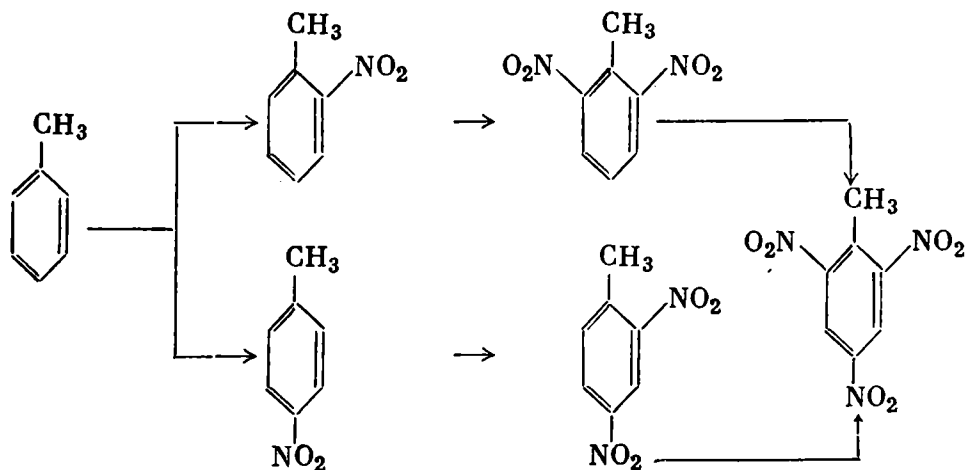
4. A nitro group introduced into a molecule of phenol or a carboxylic acid makes the acidic properties of the substance more pronounced. For instance, the ionization constant of *o*-nitrobenzoic acid is a thousand times greater than the ionization constant of benzoic acid.

In this way the introduction of the nitro group exerts a marked influence on the reactivity of a substance; it has a considerable effect on the properties of the hydrogen atoms of the benzene ring and their substituents. This will be understood when it is recalled that the nitro group, as a substituent of the second class, attracts electrons and diminishes the electron density of the benzene ring.

221. Some Representative Nitrogen Compounds. *Nitrobenzene* $C_6H_5NO_2$ is a yellowish liquid (relative density 1.203 at 20°). It has an odour resembling that of bitter almonds and is poisonous, especially as a vapour. Very large quantities of it are prepared and are used chiefly to manufacture aniline (p. 447).

Nitrations are carried out in big boilers usually constructed of cast iron and called nitrators (Fig. 64). A nitrator is fitted with a stirrer. Internal cooling coils are used to cool the reaction mixture. Cooling can also be effected by running water between the double walls of the nitrator.

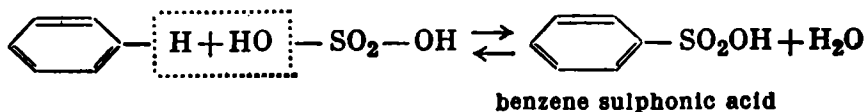
Trinitrotoluene, *trotyl*, or *TNT*, $CH_3C_6H_2(NO_2)_3$, is prepared by nitrating toluene. At first this yields *o*- and *p*-nitrotoluenes, then dinitrotoluenes, and, finally, trinitrotoluene:



Trinitrotoluene forms yellow needles (m.p. 80.1°). It is highly explosive and is used as bursting charge. Although discovered in 1863, it was first used as an explosive in 1905.

222. Sulphonation and Sulphonic Acids. The action of concentrated sulphuric acid upon aromatic compounds characterizes them as much as the reaction of nitration.

The reaction between benzene and sulphuric acid is expressed by the equation:



As can be seen from this equation, the benzene ring loses one atom of hydrogen, while the molecule of sulphuric acid gives up its hydroxyl. The released valencies of the carbon atom and the sulphur atom saturate each other. The reaction product is benzene sulphonic acid, in which a carbon atom of the benzene ring is linked to the sulphur atom.

The introduction of the SO_3H group by the action of sulphuric acid is called *sulphonation*. The reaction of sulphonation is reversible, and a large excess of concentrated sulphuric acid should therefore be taken to make as much as possible of the benzene react. Fuming sulphuric acid (oleum) can also be used, but it should be borne in mind that high-percentage oleum can cause the formation of *m*-disulphonic acid.

The apparatus in which sulphonation is conducted is called a sulphonator (Fig. 65). It is a cast-iron cylindrical boiler with a convex bottom, surrounded by steam jacket 1; in the lid of the sulphonator there is the charging manhole 2. The reacting mass is stirred by impeller 3. The pressure inside the sulphonator is measured by gauge 4; the temperature, by the thermometer in well 5.

Sulphonators usually have a volume of 1.5-5 cu m.

Benzene sulphonation is carried out in the same way, its vapours being led through sulphuric acid placed in a special sulphonator.

The sulphonic acids are colourless crystalline substances readily soluble in water. Unlike the carboxylic acids, they are strong acids, since their acidic properties are due to the presence of a strong acid (sulphuric) residue. Their sodium salts usually have a low solubility in a saturated sodium chloride solution.

Other aromatic compounds (hydrocarbons, acids, etc.) can be sulphonated, as well as benzene. For instance, the sulphonation of tolu-

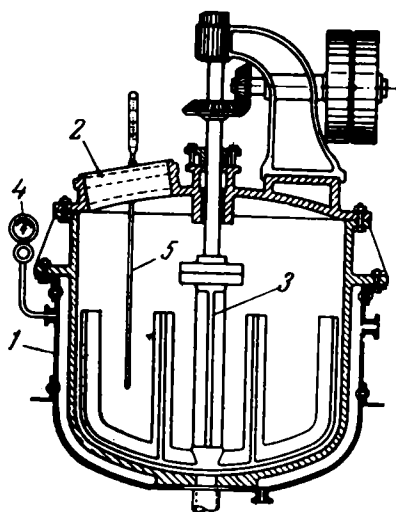
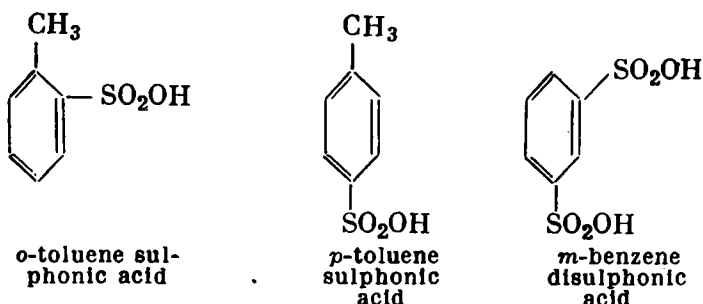


Fig. 65. Sulphonator (cross-section):

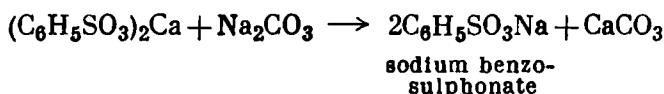
1—steam jacket; 2—charging manhole; 3—impeller; 4—pressure gauge; 5—thermometer well.

ene produces *o*- and *p*-toluene sulphonic acids:



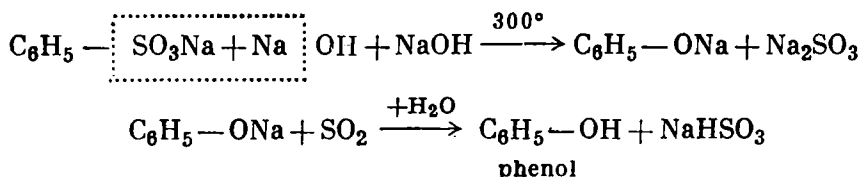
By vigorous sulphonation it is possible to introduce two or three sulphonyls $-\text{SO}_3\text{H}$, instead of one, into the benzene ring; in this way it is possible to prepare the important *m*-benzene disulphonic acid.

The reaction products in sulphonations are usually mixed with surplus sulphuric acid. The industrial process of separating them from the acid is known as the "lime-out" operation. The reaction mixture is diluted with water, neutralized with lime, and filtered. The filter collects the calcium sulphate, while the filtrate contains the readily soluble calcium benzenesulphonate $(\text{C}_6\text{H}_5\text{SO}_3)_2\text{Ca}$. The filtrate is treated with soda, whereupon the solution is filtered again to separate the precipitated calcium carbonate:



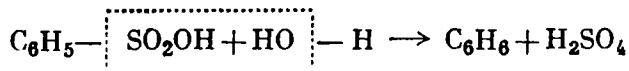
The filtrate containing the soluble sodium salt of benzenesulphonic acid is evaporated to yield crystalline sodium benzenesulphonate.

It is typical of sulphonic acids that a hydroxyl, hydrogen, or a nitrile group can be substituted for the sulphonyl group. For example, the fusion of the sodium salt of a sulphonic acid with an alkali produces phenol:



The reaction serves to prepare many phenols.

When sulphonic acids are treated with superheated steam, especially under pressure, the sulphonyl breaks away and an aromatic hydrocarbon is formed:

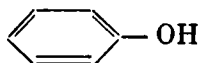


The sulphonation products of the aromatic hydrocarbons are highly important in the preparation of certain derivatives (phenols, aromatic acids, etc.). In addition to this, the sulphoxyl is often introduced into the molecule to make a compound water-soluble. Benzene sulphonic acid and toluene sulphonic acid are sometimes used as catalysts (e.g., in esterification) instead of sulphuric acid which causes undesirable side processes.

PHENOLS AND AROMATIC ALCOHOLS. QUINONES

223. Structure of Phenols, Their Preparation and Properties. Earlier we established the difference between halogen derivatives in which the halogen is linked to the benzene ring and compounds with the halogen in the side chain. Similarly there is a considerable difference between substances in which a hydroxyl is linked to the ring and substances with a hydroxyl in the side chain.

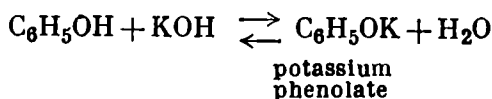
Compounds containing hydroxyls attached to carbon atoms of the benzene ring are called phenols. The simplest of the phenols, the monohydroxy derivative of benzene, is known by the name given to this class of compounds. *Phenol*, or, as it is also called, *carbolic acid*, has the formula:



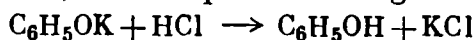
Phenols may be synthesized by the following methods:

1. By fusing sulphonic acid salts with alkalis.
2. By decomposing diazonium salts in certain conditions (p. 463).
3. By treating halogen derivatives of benzene hydrocarbons with alkali solutions at a high temperature.

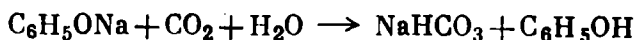
Phenols are faintly acidic. Whereas alcohols produce alcoholates only when treated with a free metal, the hydrogen of the phenol hydroxyl can be replaced not only by the action of a metal, but also by treating the phenol with a caustic alkali. The resulting substances are called *phenolates*:



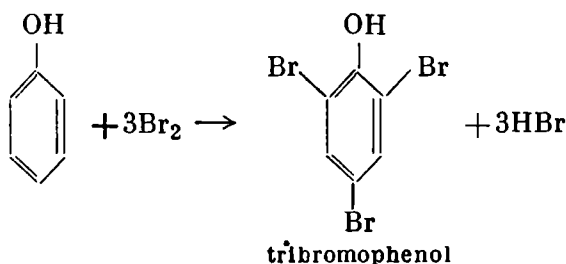
Since phenolates are soluble in water, phenols, which are themselves insoluble, dissolve when treated with alkalis, whereas alcohols insoluble in water do not dissolve in alkalis either. The acidic properties of phenols are, however, very faint, and phenolates are decomposed by dilute acids, a free phenol being formed:



Even carbonic acid decomposes phenolates, producing free phenol:



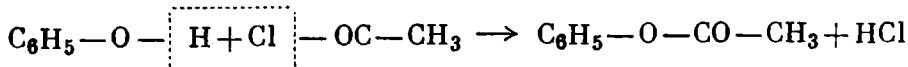
The phenyl radical and the hydroxyl group have a certain mutual influence upon each other: the effect of the phenyl radical is to impart acidic properties to the hydroxyl group. The acidity of the phenol hydroxyl becomes especially pronounced under the influence of electronegative groups, such as $-\text{NO}_2$. The nitrophenols are stronger acids (p. 421) than phenol or its homologues. On the other hand, the hydroxyl group lends greater mobility to the hydrogen atoms of the benzene ring, and they become more easily replaceable. For instance, catalysts have to be used to substitute bromine for hydrogen in benzene, whereas in phenol the substitution of bromine for benzene ring hydrogen atoms can be effected very easily even by treatment with bromine water:



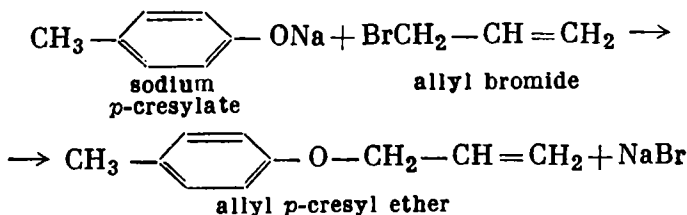
The halogen atoms in this case assume para-ortho-positions with respect to the OH group, which has a marked orienting effect of the first class.

Phenol is nitrated and sulphonated more readily than benzene. As in the previous reaction, the nitro and sulfoxyl groups assume ortho-para-positions with respect to the OH group. When, for example, phenol is treated with dilute nitric acid, the product is a mixture of *p*- and *o*-nitrophenols. The *o*-nitrophenol can be easily isolated from the mixture by steam distillation (p. 24). The para-isomer is not carried over with the steam.

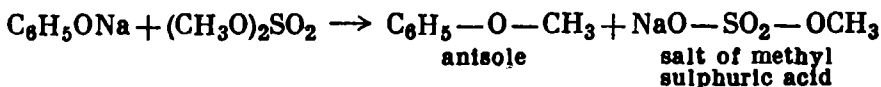
Certain esters of phenols are known, such as $\text{C}_6\text{H}_5\text{O}-\text{COCH}_3$. They can be prepared by treating phenols with acid chlorides or anhydrides:



Ethers of phenols are prepared by the action of alkyl halides on phenolates of alkali metals:



Methyl and ethyl ethers are usually prepared by means of methyl or ethyl sulphate:

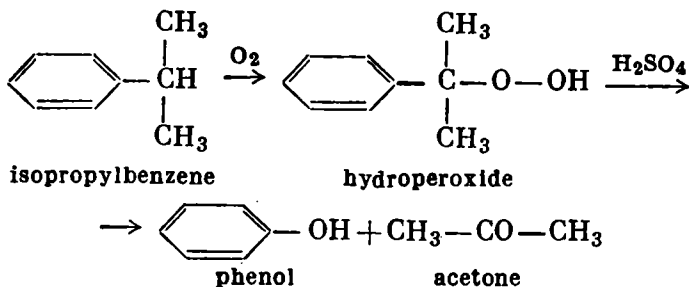


The phenol hydroxyl, unlike the alcohol hydroxyl, is not easily replaced by a halogen.

Solutions of most of the phenols give characteristic colour reactions with ferric chloride.

224. Phenol. Cresols. *Phenol* $\text{C}_6\text{H}_5\text{OH}$ is a colourless crystalline substance, melting at 42.3° and boiling at 182° ; on standing exposed to air, it becomes pink and, finally, brown, owing to oxidation. Phenol has a characteristic, highly intense odour. It has a poor solubility in water. It crystallizes as the monohydrate $\text{C}_6\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$, which melts at 16° . When water is added to phenol, two layers are formed: the lower layer is a solution of water in phenol, while the upper is a solution of phenol in water. With a rise in temperature there is an increase in the solubility of both the water in the phenol and the phenol in the water; at 68° they become miscible in any proportion. With ferric chloride, phenol gives a violet colour reaction. Phenol is contained in coal-tar, wood-tar, and peat-tar. The amount of phenol obtained from tar meets only part of the demand, and the bulk of the product is now therefore made synthetically: either by fusing the sodium salt of benzene sulphonic acid with sodium hydroxide or by heating chlorobenzene with water and lime to 350° .

A new method for making phenol is by oxidizing isopropylbenzene (cumene); this also yields acetone:



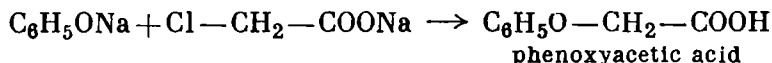
Phenol is a most important industrial semi-product. It is used in the manufacture of plastics, picric acid, salicylic drugs, dyes, etc. The phenol ethers—anisole $\text{C}_6\text{H}_5\text{OCH}_3$ (b.p. 153.8°) and phenetole $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ (b.p. 172°)—are liquids with pleasant odours; they are insoluble in water or in aqueous solutions of alkalis.

Phenol is a normal product of the metabolism; in the form of phenyl sulphates, such as $\text{C}_6\text{H}_5\text{OSO}_2\text{ONa}$, it is contained in urine.

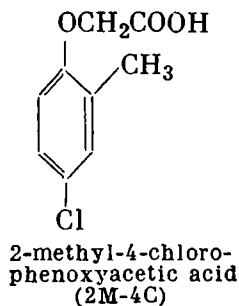
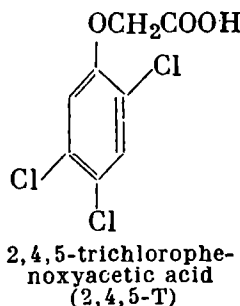
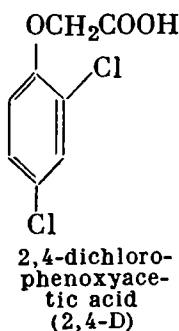
The closest homologues of phenol are the *cresols* $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$, or hydroxytoluenes. They are prepared from coal-tar. Para-cresol is one of the products of protein putrefaction.

All the phenols are strong bactericidal agents even in very weak solutions. For this reason phenol and the cresols are used extensively in medicine and veterinary practice as disinfectants. In the pure state and in concentrated solutions they cause blisters that do not heal for a long time. A very frequently used disinfectant is *lysol*, a soap solution of a mixture of *o*-, *m*-, and *p*-cresols prepared from coal-tar and from the products of the dry distillation of wood and peat.

225. Plant Growth Regulators and Herbicides. Many substances even in very small quantities have a marked influence on plants. Their effect on plants can be very different. There are especially many substances that considerably accelerate seed germination and root development. These substances are usually called *plant growth regulators*. One natural substance of this type is indole acetic acid, or heteroauxin (p. 547). The derivatives of phenoxyacetic acid have acquired extensive practical applications. They can be prepared by the general method of treating corresponding sodium phenolates with the sodium salt of chloroacetic acid:



The compounds of practical importance are:



The action of even very weak solutions (0.001%) of these substances on the root system, and also on the leaves, considerably accelerates the development of the roots and, hence, of the plant as a whole. If, however, these substances are applied in large concentrations, far from promoting growth, they inhibit a plant's development and can even cause it to perish. The dicotyl plants (which include many weeds) are the more sensitive to such concentration

risks, whereas the monocotyledonous plants (cereals) are resistant to these substances. Thanks to this fact, these substances can be used as *herbicides*, or weed-killers, which makes possible the chemical weed control of wheat, rye, and other crops. This is accomplished by either ground or aerial spraying. Inasmuch as these substances are inexpensive and such treatment requires little labour, their use furnishes a very efficient means of weed control.

The same substances (2,4-D and others) are also used with success to facilitate the rooting of ligneous plants. The spraying of the young fruit of orchard and garden plants increases their yield, while in the case, say, of tomatoes it hastens ripening and produces a pit-less fruit.

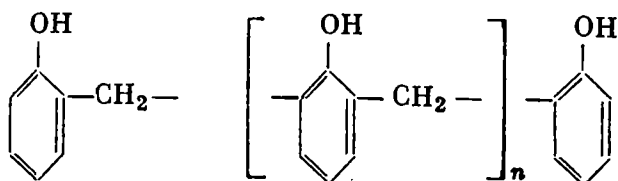
226. Phenol-Formaldehyde Resins. In the seventies of the past century it was found that a condensation reaction is possible between phenol and formaldehyde, resulting in resin-like substances. But the first artificial resins to find practical application appeared only in 1902, i.e., thirty years later.

The resins were obtained by a phenol-formalin polycondensation reaction with heating in the presence of acids:

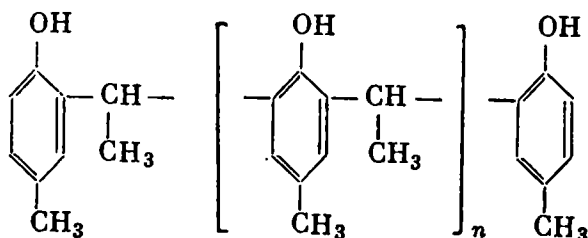


where $n = 4, 5, \dots 8$. They were found to have an excellent solubility in alcohol and, under the name of "novolacs", soon came to have many uses. Highly diverse resins are prepared today by heating phenols with aldehydes. Some are soluble in alcohol; others, in oils.

The structural formula of phenol-formaldehyde novolac is:



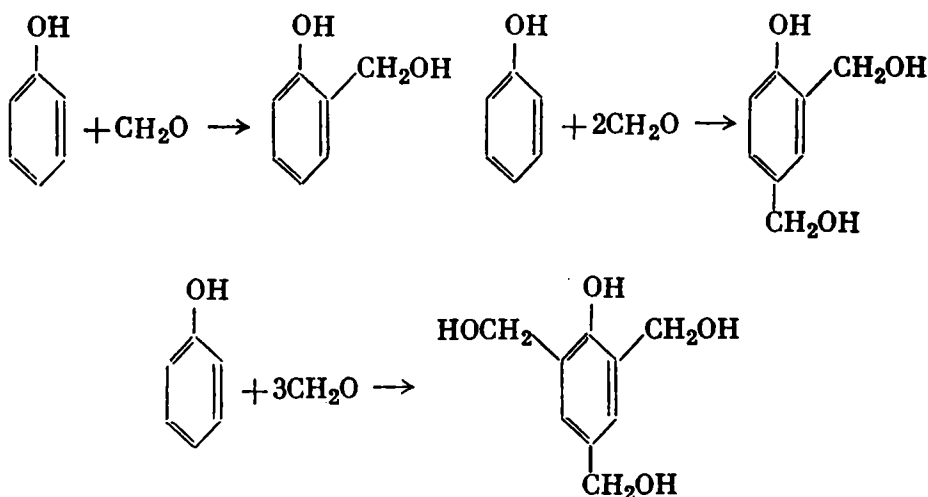
Para-cresol-acetaldehyde novolac has the formula:



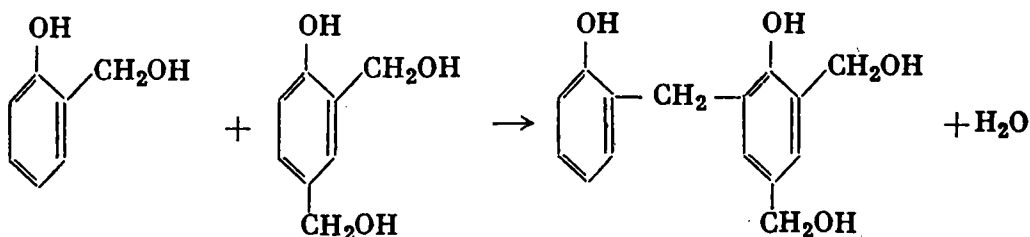
The novolacs are therefore polycondensation products and have a linear structure.

Thermosetting resins were discovered in 1907. These are resins that upon heating harden, or set, to become infusible plastics that are practically insoluble in all solvents. Typical of such plastics is *bakelite*. It is made by heating phenol with formalin in the presence of ammonia. A thick mass is precipitated after a time, and this then turns into a resin (resol), which softens at 50-60°. Subsequent more intense heating converts it into a solid infusible and insoluble substance (resite). The general pattern of the formation of resol and resite can be represented as follows.

At first phenol and formaldehyde react in the presence of an alkali catalyst to form a mixture of phenol alcohols:

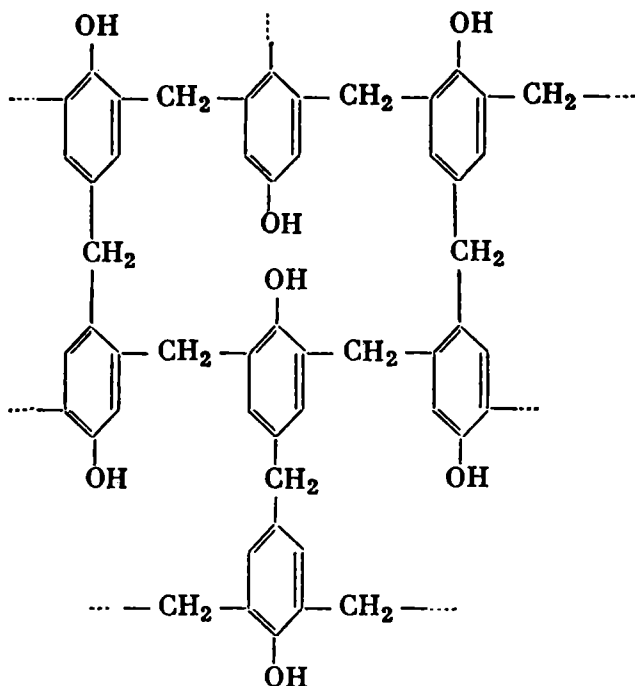


The phenol alcohol molecules then condense, losing water and forming linear molecules of resol:



etc.

This is followed by the condensation of the resol molecules and the formation of the solid polymer resite:

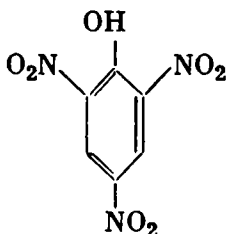


Resite has a reticulate spatial macromolecule.

The novolac resins can be converted into resol resins and resite by the addition of formaldehyde or hexamethylenetetramine (urotropine) and heating.

Phenol-formaldehyde resins and the plastics based upon them, called *phenoplasts*, were the first type of plastics to become widespread. They are used to make numerous electrical fittings and radio parts, telephones and telephone receivers, machine parts, pinions, and household goods. An important application of the resins is as a binding agent in making fibre board and ply-wood. Despite the emergence of new types of plastics, phenol-formaldehyde resins have not lost their usefulness and continue to be produced in large quantities. This is because they are readily available, inexpensive, and serve many purposes.

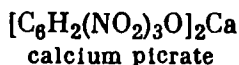
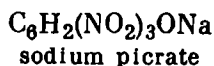
227. Picric Acid. Picric acid (2,4,6-trinitrophenol)



is prepared by nitrating phenol. It is a solid crystalline substance

melting at 122° ; it has a bitter taste. At one time it was used as a yellow dye for wool and silk.

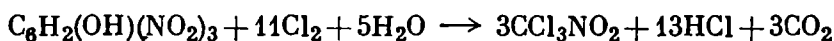
Picric acid has pronounced acidic properties. Its hydroxyl hydrogen can be replaced by a metal; the resulting picric acid salts are called *picrates*:



Picric acid is an explosive; under the names of lyddite, melinite, and shimose it has been used for filling artillery shells.

Its drawback as an explosive is the fact that its salts, especially lead picrate, are very sensitive; this makes the production of picric acid and the filling of shells with it highly dangerous.

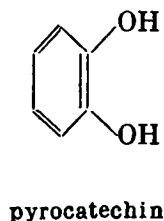
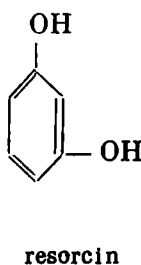
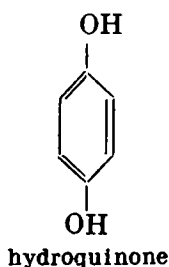
Picric acid is the material from which chloropicrin is made. Chloropicrin is formed when an alkaline solution of picric acid is treated with chlorine:



Chloropicrin is a liquid boiling at 112° ; its vapour acts as a powerful lachrymator and is poisonous.

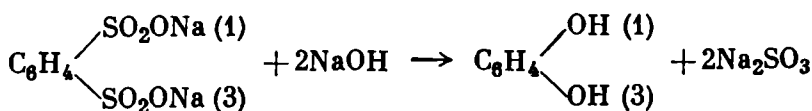
228. Dihydric Phenols. The simplest of the dihydric phenols are the dihydroxy derivatives of benzene, which are called the dihydroxybenzenes $\text{C}_6\text{H}_4(\text{OH})_2$.

All three theoretically possible isomers are known: *p*-dihydroxybenzene (hydroquinone), *m*-dihydroxybenzene (resorcin), and *o*-dihydroxybenzene (pyrocatechin):



Hydroquinone is prepared by reducing quinone (p. 424); it is used as a photographic developer.

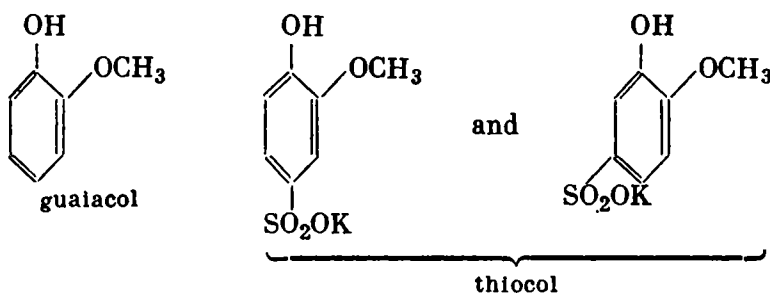
Resorcin is prepared by fusing *m*-benzene disulphonic acid with sodium hydroxide:



It is used in synthesizing certain dyes.

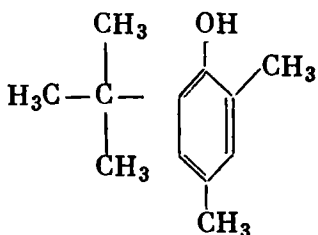
Pyrocatechin was first obtained by the destructive distillation of various species of the tropical plant catechu. It is synthesized by heating a mixture of *o*-chlorophenol with a dilute solution of sodium hydroxide and a small amount of blue vitriol to 196°.

The monomethyl ether of pyrocatechin is called *guaiacol*; large quantities of it are contained in beechwood tar. Guaiacol and the potassium salt of its sulphonic acids (*thiocol*) are used medicinally in the treatment of respiratory diseases:

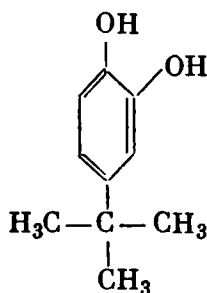


The dihydric phenols are crystalline substances. With ferric chloride they give bright colours: pyrocatechin, a green colour; resorcin, violet, and hydroquinone, a dirty green, which, owing to oxidation with the further addition of the reagent, turns to yellow. The dihydric phenols are readily oxidized in an alkaline solution by the oxygen of the air. Their oxidation by silver nitrate causes metallic silver to be deposited. Resorcin undergoes oxidation with greater difficulty than the others.

Antioxidants. Many alkylphenols have found extensive application as negative catalysts of oxidation reactions. Such substances have been called antioxidants or oxidation retarders. The following two compounds are the most widely used:

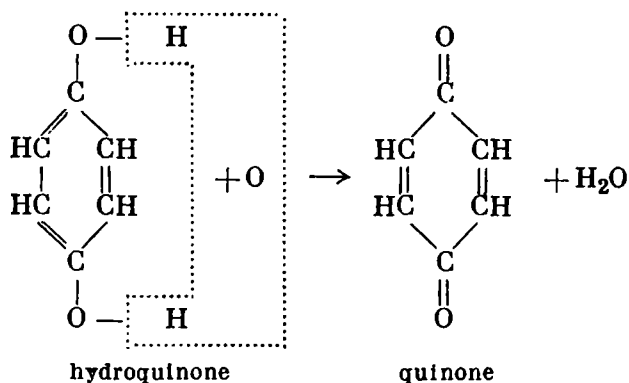


2,4-dimethyl-6-ter-butylphenol. Petrol oxidation retarder



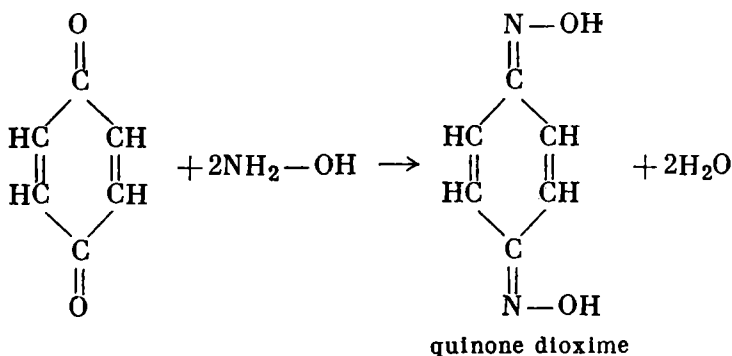
n-ter-butyl-pyrocatechol. Retarder of divinyl polymerization (caused by oxidation during storage)

229. Quinones. The oxidation of hydroquinone produces golden yellow crystals of quinone $C_6H_4O_2$:



As can be seen from the above formula, quinone is a ketone; furthermore, its ring does not contain the alternate single and double bonds typical of benzene.

Such a structure of quinone is confirmed by the fact that a single molecule of quinone adds four atoms of bromine or chlorine, and by the fact that it reacts with hydroxylamine to form a *dioxime*:



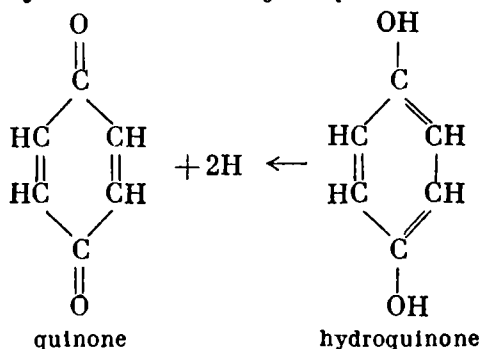
A system of double bonds such as in the quinone molecule is called *quinonoid*:



A quinonoid structure is characteristic of many dyes.

Quinone was discovered by A. Voskresensky in 1838. It has a pungent odour, melts at 116° , and sublimes easily.

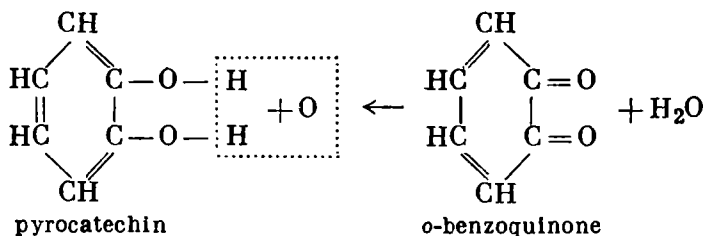
Quinone is readily reduced to *hydroquinone*:



Quinone is prepared by the oxidation of aniline.

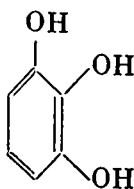
With phenols it forms brightly coloured compounds. A molecule of quinone combines with a molecule of hydroquinone to form the compound *quinhydrone*, pretty dark green crystals.

Other Quinones. The quinone described above should more correctly be called *p*-benzoquinone. There are several other quinones, in which the oxygen atoms are in *p*- or *o*-position. For example, the gentle oxidation of pyrocatechol yields *o*-benzoquinone:

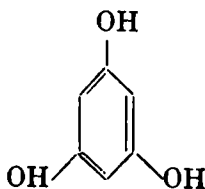


The *p*-quinones are the most important in this group. They are of a golden yellow colour, have a characteristic pungent odour, and can be distilled with steam. There are no *m*-quinones, which is in full conformity with the structure of benzene.

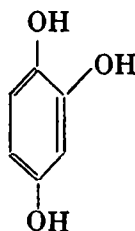
230. Trihydric Phenols. All three theoretically possible trihydroxybenzenes are known: vicinal trihydroxybenzene, or pyrogallol; symmetric trihydroxybenzene, or phloroglucinol, and asymmetric trihydroxybenzene, or hydroxyhydroquinone:



1,2,3-trihydroxybenzene
(pyrogallol)



1,3,5-trihydroxybenzene
(phloroglucinol)



1,2,4-trihydroxybenzene
(hydroxyhydroquinone)

All three are crystalline substances.

Pyrogallol is usually prepared by heating gallic acid (p. 443), which gives up carbon dioxide. In an alkaline solution, pyrogallol is readily oxidized by the oxygen of the air. To demonstrate how readily it oxidizes, a small amount of pyrogallol should be put in a flask, a solution of sodium hydroxide added, and the flask closed quickly with a cork connected by tube with a glass containing some coloured water (Fig. 66). When the flask is shaken, the pyrogallol rapidly begins to turn brown, while the water begins to rise in the tube, taking the place of the oxygen used up in oxidizing the pyrogallol.

Pyrogallol is used as a photographic developer, as well as in gas analysis for the determination of oxygen in mixtures with other gases.

Phloroglucinol can be prepared by fusing many natural resins with potassium hydroxide. It crystallizes with two molecules of water, has a sweet taste, and gives a dark violet colour with ferric chloride. Phloroglucinol is often regarded as a tautomeric compound. It reacts either as a trihydric phenol or as a cyclic triketone (triketo-hexamethylene):

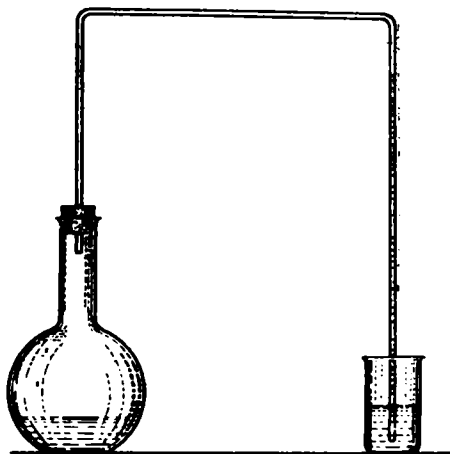
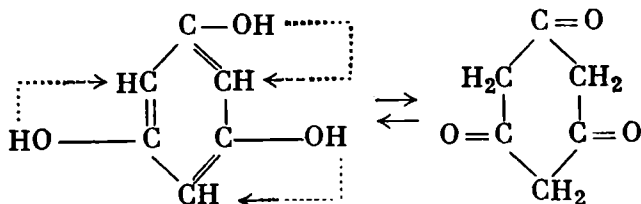


Fig. 66. Apparatus for demonstrating the absorption of atmospheric oxygen by pyrogallol.



As a triketone, phloroglucinol reacts with hydroxylamine, yielding a trioxime; as a trihydric phenol, on the other hand, it reacts with acetyl chloride to yield the ester $\text{C}_6\text{H}_3(\text{OCOCH}_3)_3$. It thus reacts both as a phenol and as a ketone.

The two tautomeric forms of phloroglucinol have not been isolated, and only one compound is known. Its absorption spectrum is like that of phenols rather than ketones, which suggests that the greater part is in phenol form.

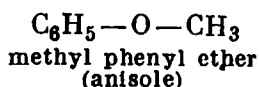
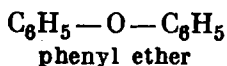
Phloroglucinol is used as a reagent for lignin. A drop of a 1% alcoholic solution of phloroglucinol gives a cherry-red colour to lignin wetted with hydrochloric acid. This reaction makes it possible to detect admixtures of lignin in cheap grades of paper.

The physical properties of the phenols are listed in Table 19.

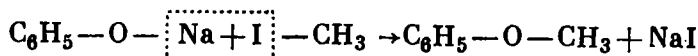
TABLE 19. Physical Properties of Phenols

Phenol	Formula	Melting point, °C	Boiling point, °C	Solubility in g per 100 g of water
Phenol	C_6H_5OH	42.3	182	8 (at 25°) miscible at 68°
<i>o</i> -Cresol	$CH_3C_6H_4OH$	31	191	3 (at 35°)
<i>m</i> -Cresol	$CH_3C_6H_4OH$	11.9	202.2	2.4 (at 25°)
<i>p</i> -Cresol	$CH_3C_6H_4OH$	35	202	2.4 (at 40°)
Pyrocatechol (1,2-dihydroxybenzene)	$C_6H_4(OH)_2$	105	245	24 (at 20°)
Resorcin (1,3-dihydroxybenzene)	$C_6H_4(OH)_2$	110	277	147 (at 20°)
Hydroquinone (1,4-dihydroxybenzene)	$C_6H_4(OH)_2$	170.5	286	6.5 (at 20°)
Pyrogallol (1,2,3-trihydroxybenzene)	$C_6H_3(OH)_3$	133	309	6.0 (at 20°)
Phloroglucinol (1,3,5-trihydroxybenzene)	$C_6H_3(OH)_3$	219	—	dissolves very well
Hydroxyhydroquinone (1,2,4-trihydroxybenzene)	$C_6H_3(OH)_3$	140.5	—	—

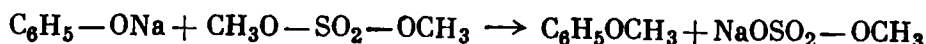
231. Aromatic Ethers. It is customary to distinguish purely aromatic ethers, such as phenyl ether, and aliphatic-aromatic ethers, in which one radical belongs to the fatty series, while the other belongs to the aromatic:



Aliphatic-aromatic ethers are produced by the interaction of halogen derivatives of hydrocarbons and phenolates:

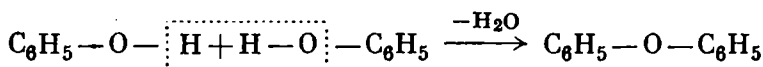


A cheaper and more convenient methylating agent is methyl sulphate, which reacts with phenols in an alkaline medium:



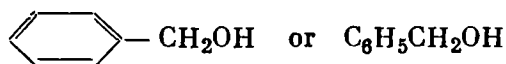
Purely aromatic ethers can be obtained by treating phenolates with aromatic halogen derivatives in the presence of powdered copper. Phenyl ether, for instance, is prepared in the presence of that catalyst by heating a mixture of bromobenzene and potassium phenolate to 210° .

Another method of preparing them is by heating phenols with dehydrating agents, such as anhydrous aluminium trichloride or zinc chloride:



232. Aromatic Alcohols. *Compounds in which a hydroxyl has been substituted for a hydrogen atom in the side chain of an aromatic hydrocarbon are called aromatic alcohols.*

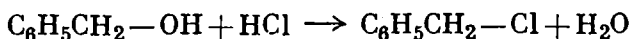
The simplest aromatic alcohol is *benzyl alcohol*:



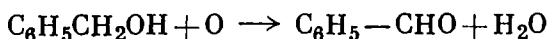
Benzyl alcohol is a liquid with a faint pleasant odour (b.p. 205.5°); it is not soluble either in water or in alkalis.

Benzyl alcohol and some of its esters are used in the perfume industry.

The aromatic alcohols possess typical properties of saturated alcohols. Benzyl alcohol, for example, forms ethers and esters; when treated with hydrogen chloride it is converted into benzyl chloride:



Benzyl alcohol can be oxidized to benzaldehyde:



The aromatic alcohols, unlike the phenols, do not give a colour reaction with ferric chloride.

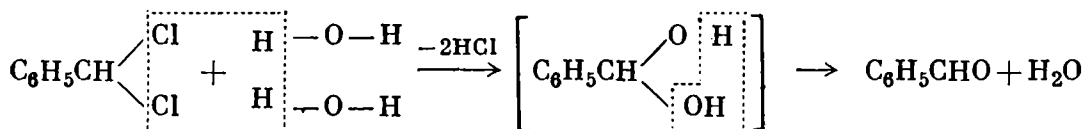
AROMATIC ALDEHYDES AND KETONES

233. Aldehydes. The simplest aromatic aldehyde is *benzaldehyde* $\text{C}_6\text{H}_5-\text{CHO}$. It occurs in nature as the glucoside amygdalin $\text{C}_{20}\text{H}_{27}\text{NO}_{11}$, which is contained in bitter almonds and in laurel-cherry leaves.

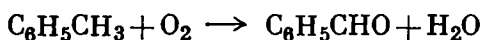
Amygdalin is hydrolyzed by the enzyme emulsin, occurring with it, to glucose, benzaldehyde, and hydrogen cyanide.

The reaction can be brought about by rubbing bitter almonds or laurel-cherry leaves with water.

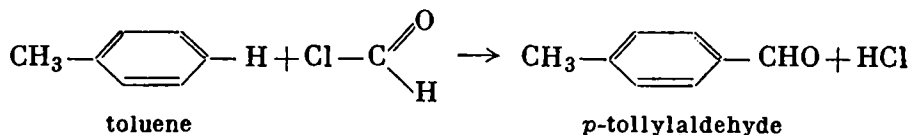
Industrially benzaldehyde is prepared from toluene. The toluene is chlorinated for this purpose. The initial product of chlorination is benzyl chloride $C_6H_5CH_2Cl$; its further chlorination yields benzylidene chloride $C_6H_5CHCl_2$. When the latter is heated with water and a small amount of calcium hydroxide or sulphuric acid, benzaldehyde is formed:



Another method of preparing benzaldehyde is by the direct oxidation of toluene by passing its vapour and air through a tube containing catalysts (iron oxides) at an increased temperature:



Homologues of benzaldehyde can be prepared by the *Gattermann reaction*: by treating aromatic hydrocarbons with carbon monoxide and dry hydrogen chloride in the presence of aluminium trichloride and cuprous chloride. The carbon monoxide and the hydrogen chloride in this case react as formic acid chloride $HCOCl$:

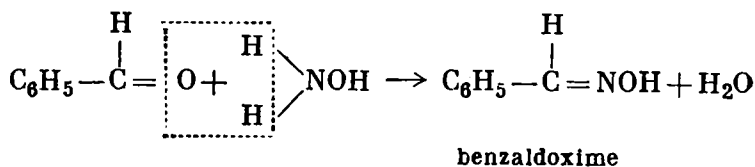


The aldehyde group in this reaction assumes a para-position in relation to the substituent in the benzene ring.

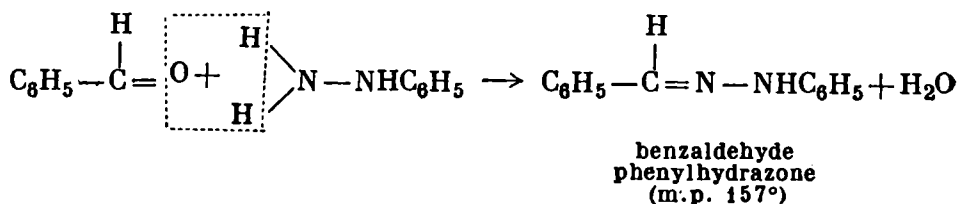
Benzaldehyde is a liquid boiling at 178.1° . It has a relative density of 1.05 and a strong odour of bitter almonds.

The following of its properties deserve mention.

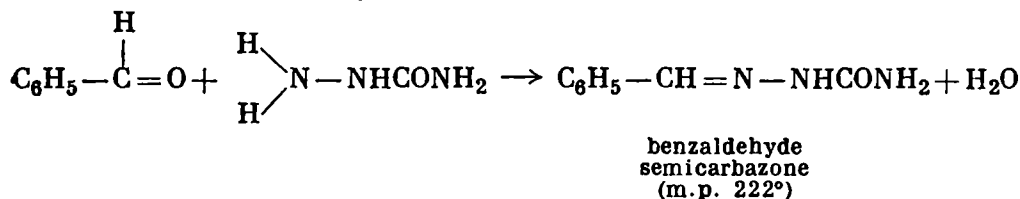
1. Benzaldehyde has the typical properties of an aldehyde of the aliphatic series. For instance, with sodium hydrosulphite it forms a crystalline addition product. With hydroxylamine it forms an oxime:



With phenylhydrazine it produces a phenylhydrazone:



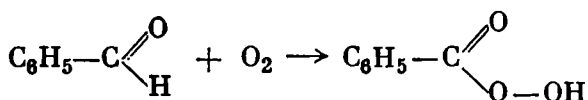
With semicarbazide it yields a semicarbazone:



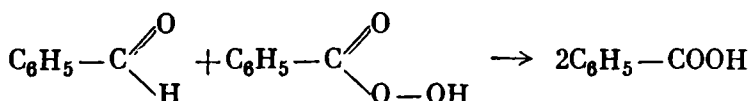
benzaldehyde
semicarbazone
(m.p. 222°)

2. The oxygen of the air oxidizes benzaldehyde quite rapidly, and it is turned into a solid mass of crystals of benzoic acid C_6H_5COOH .

The mechanism of the reaction is such that benzaldehyde absorbs oxygen to form an intermediate compound, which in all probability is *benzoyl hydrogen peroxide*:

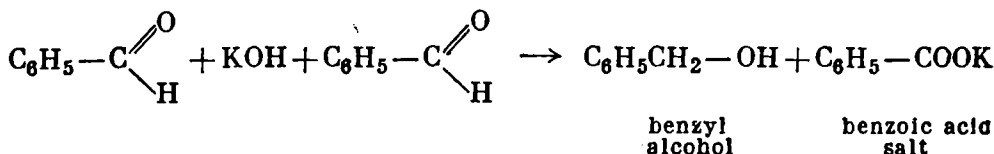


The benzoyl hydrogen peroxide then oxidizes the rest of the benzaldehyde to benzoic acid:



This initial formation of peroxides is typical of *auto-oxidation reactions*, i.e., of the oxidation of various substances by gaseous oxygen, which takes place even at room temperature. If, together with the substance capable of auto-oxidation, we introduce some substance that undergoes oxidation readily, it will be oxidized by the peroxide formed; in other words, the oxygen of the air will be activated. That is why the presence of benzaldehyde brings about the oxidation of certain substances (e.g., indigo sulphonic acid) ordinarily unaffected by oxygen. The amount of oxygen expended on oxidizing the substance introduced is that needed to oxidize the benzaldehyde to benzoic acid, which is in agreement with the above equations.

3. Benzaldehyde, like other aldehydes that do not contain an α -hydrogen atom, is not resinified by alkalis. Under the influence of alkali solutions it forms benzyl alcohol and benzoic acid:

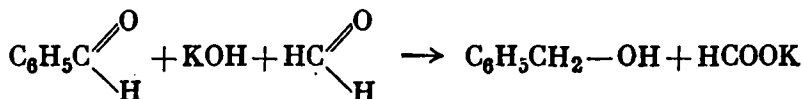
benzyl
alcohol

benzoic acid
salt

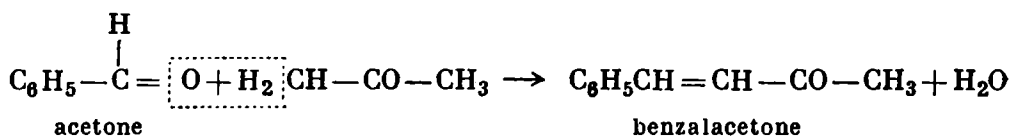
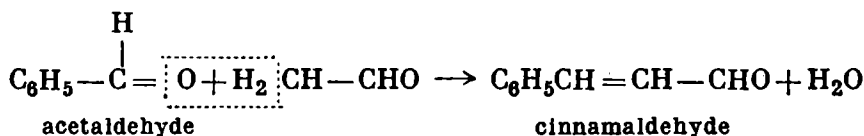
This reaction was discovered by Cannizzaro in 1853.

If a mixture of an aromatic aldehyde and formaldehyde is taken for the reaction, formic acid and the corresponding aromatic alcohol

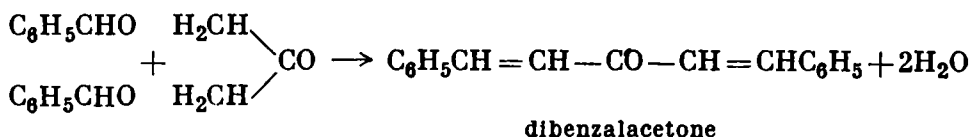
are formed (V. Rodionov, 1936):



4. Benzaldehyde condenses readily with other substances. It reacts with aldehydes, ketones, and acids of the fatty series that have two hydrogen atoms attached to the α -hydrogen atom to yield substances with an unsaturated side chain:

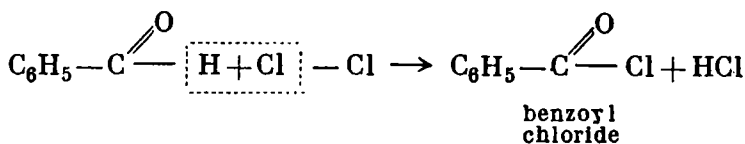


Benzaldehyde condenses with acetone in the presence of sodium hydroxide. According to the proportion in which the reagents are taken, the product is either benzalacetone or dibenzalacetone:

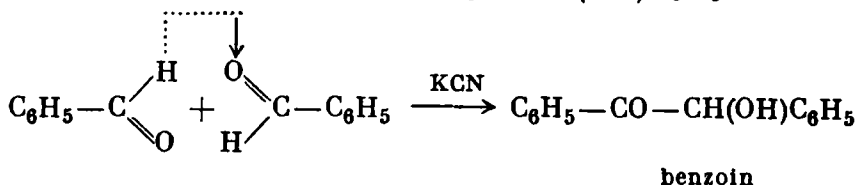


Benzalacetone forms light yellow crystals, which have a pleasant odour; it is used in the perfume industry. *Dibenzalacetone* is a yellow crystalline substance, easily isolated and identified by its melting point (112°). For this reason the reaction of dibenzalacetone formation can be used for identifying small quantities of acetone.

5. Treatment with chlorine converts benzaldehyde to benzoyl chloride:



6. In the presence of potassium cyanide as a catalyst, benzaldehyde is converted to *benzoin* $\text{C}_6\text{H}_5\text{COCH}(\text{OH})\text{C}_6\text{H}_5$:



In this reaction the hydrogen atom of the aldehyde group of one benzaldehyde molecule shifts to the oxygen atom of the aldehyde

group of another benzaldehyde molecule. Both aldehyde groups in this way find themselves with free carbon atom valencies, and these saturate each other.

Benzoin is a colourless crystalline substance melting at 137° . It was first prepared by N. Zinin in 1839. Its oxidation (for example, by concentrated nitric acid) produces the diketone *benzil* $\text{C}_6\text{H}_5\text{—CO—CO—C}_6\text{H}_5$. This is a yellow crystalline substance, which melts at 95° .

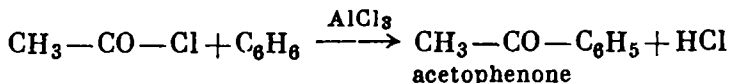
Benzaldehyde is used to make perfumes and dyes.

It might appear that the Cannizzaro reaction and the benzoin condensation reaction distinguish aromatic aldehydes radically from aliphatic aldehydes. But on closer scrutiny it will become apparent that the different attitude of the aromatic and aliphatic aldehydes to alkalis is not due to the properties of the aldehyde group itself, but may be traced to the active α -hydrogen atom in the aliphatic aldehydes. Earlier we saw that the action of alkalis on formaldehyde (which has no α -hydrogen) turns it into formic acid and methanol; a similar conversion of acetaldehyde into an acid and an alcohol takes place in the fermentation reaction (p. 310). In several other biological processes acetaldehyde is converted to acetoin $\text{CH}_3\text{COCH(OH)CH}_3$.

234. Ketones. The carbonyl group in aromatic ketones may be linked either to two aromatic radicals or to an aromatic radical and an alkyl; i.e., a radical of the aliphatic series.

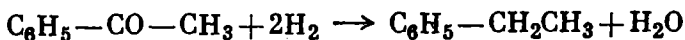
Methyl phenyl ketone (*acetophenone*) $\text{C}_6\text{H}_5\text{COCH}_3$ is an example of the latter group; diphenyl ketone (*benzophenone*), of the former group.

Aromatic ketones may be Friedel-Crafts synthesized by the action of acid chlorides upon aromatic hydrocarbons in the presence of anhydrous aluminium trichloride:

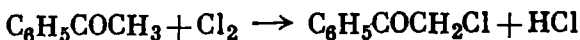


With hydroxylamine the aromatic ketones, like their aliphatic counterparts, form oximes, while with phenylhydrazine they produce phenylhydrazones.

Amalgamated zinc and concentrated hydrochloric acid reduce aromatic-aliphatic ketones to benzene homologues:



Chloroacetophenone $\text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$, a derivative of acetophenone, is one of the most highly lachrymatory chemical warfare agents. It is prepared by the action of chlorine upon acetophenone:

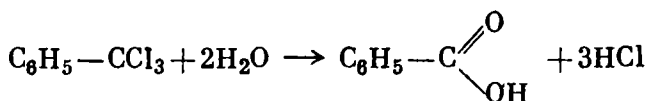


Chloroacetophenone is a crystalline substance (m.p. 52°) with an odour of violets.

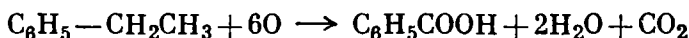
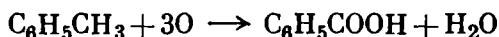
AROMATIC CARBOXYLIC ACIDS

235. Benzoic Acid. Benzoic acid $\text{C}_6\text{H}_5\text{—COOH}$ occurs in certain gums; its derivative hippuric acid $\text{C}_6\text{H}_5\text{CONHCH}_2\text{COOH}$ is found in the urine of horses.

Industrially benzoic acid is prepared from toluene. The full chlorination of the toluene side chain yields benzotrichloride (phenyltrichloromethane) $\text{C}_6\text{H}_5\text{CCl}_3$. When this is heated with water, benzoic acid is formed:

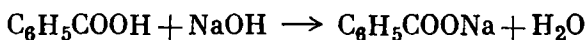


Benzoic acid is likewise obtained by oxidizing aromatic hydrocarbons with a single side chain:

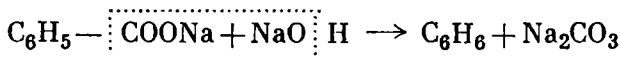


Benzoic acid is a crystalline substance melting at 122.4° . It is easily sublimed and forms white plates. Poorly soluble in water, it becomes much more soluble with a rise in temperature. As an acid, it is somewhat stronger than acetic acid (the ionization constants are 6.8×10^{-5} and 1.8×10^{-5} respectively).

In chemical properties benzoic acid is similar to the aliphatic carboxylic acids. With bases it too forms salts. Its salts with alkaline metals are readily soluble in water, and for this reason benzoic acid dissolves in alkalis:

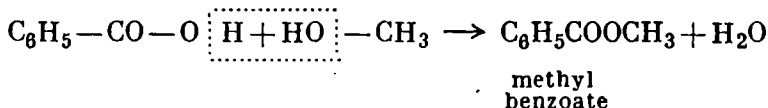


When sodium benzoate is fused with sodium hydroxide, benzene is formed:



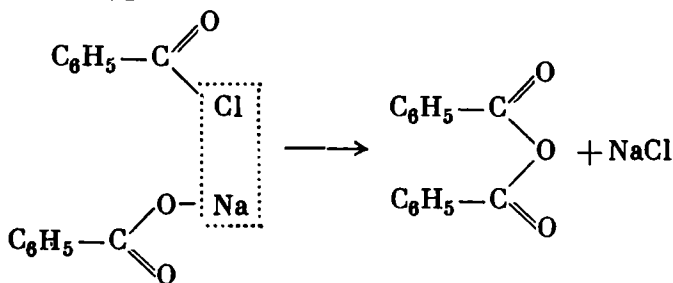
This reaction is analogous to the preparation of methane from sodium acetate and sodium hydroxide.

With alcohols, benzoic acid forms esters:

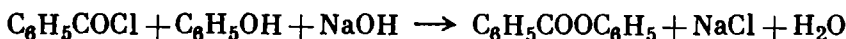


Treatment with phosphorus chlorides converts benzoic acid into the acid chloride $\text{C}_6\text{H}_5\text{COCl}$, which is called benzoyl chloride. From this compound and sodium benzoate it is possible to obtain benzoic

anhydride $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$:



Benzoyl chloride is a liquid with a pungent odour, which boils at 198° . It reacts readily as an acid chloride, but does this less violently than acetyl chloride. Benzoyl chloride is often used to introduce the benzoyl group into the molecules of alcohols, phenols, and amines. When, for example, benzoyl chloride is shaken with an alkaline solution of phenol, solid phenyl benzoate is easily formed:



Benzoic acid and its salts are used medicinally. Considerable quantities of it are also used in the synthesis of dyes and as a preservative for foods.

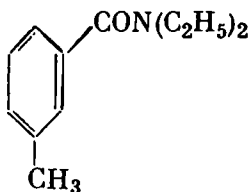
The benzoic acid radical $\text{C}_6\text{H}_5\text{CO}-$ is called *benzoyl*.

Several derivatives of benzoic acid were prepared in 1832 by Wöhler and Liebig in their investigation of the oil of bitter almonds (benzaldehyde).

By treating benzaldehyde $[\text{C}_7\text{H}_5\text{O}]\text{H}$ with chlorine or bromine, they obtained benzoyl chloride $[\text{C}_7\text{H}_5\text{O}]\text{Cl}$ and benzoyl bromide $[\text{C}_7\text{H}_5\text{O}]\text{Br}$, which, upon treatment with potassium iodide or potassium cyanide, yield benzoyl iodide $[\text{C}_7\text{H}_5\text{O}]\text{I}$ or the nitrile $[\text{C}_7\text{H}_5\text{O}]\text{CN}$ respectively. With ammonia, benzoyl chloride and benzoyl bromide yield benzamide $[\text{C}_7\text{H}_5\text{O}]\text{NH}_2$, while with alcohol they yield ethyl benzoate. Liebig and Wöhler's paper was highly important at the time. It demonstrated that all the substances they had prepared contained the radical $\text{C}_7\text{H}_5\text{O}$, which they named *benzoyl* and which was an unchanging constituent passing from one compound to another.

Benzoic amide, or *benzamide*, $\text{C}_6\text{H}_5\text{CONH}_2$ is a crystalline substance, which melts at 130° . It is prepared by the same methods as the amides of fatty acids (p. 248).

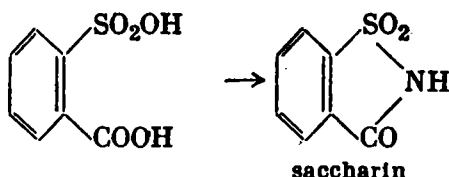
Some amides of benzoic acid and its homologues are used as *repellents* (p. 436). These substances have a prolonged repellent effect on blood-sucking insects and ticks. For example, diethyltoluamide (DETA)



is effective for 5-8 hours.

236. Saccharin. One of the compounds containing both a carboxyl and a sulphonyl is *o*-sulphobenzoic acid.

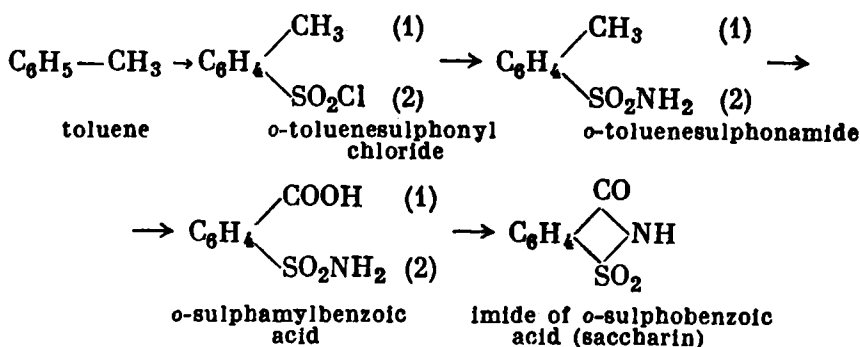
A derivative of this acid is saccharin:



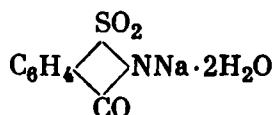
Such cyclic amides of diacids containing the $>\text{NH}$ group are called *acid imides*.

Saccharin cannot be prepared from benzoic acid, since the carboxyl is a second-class substituent and the sulphonation of benzoic acid therefore yields *m*-sulphobenzoic acid almost exclusively.

To prepare saccharin, toluene is treated with chlorosulphonic acid ClSO_2OH . This yields a mixture of *o*- and *p*-toluenesulphonyl chlorides. Intense cooling causes the *p*-isomer, which has a higher melting point, to form crystals, which can be separated from the liquid *o*-isomer. The *o*-toluenesulphonyl chloride is then treated with ammonia, which converts it to *o*-toluenesulphonamide. Oxidation with potassium permanganate converts the methyl group to a carboxyl. The product, *o*-sulphamylbenzoic acid, loses water upon heating to become saccharin:



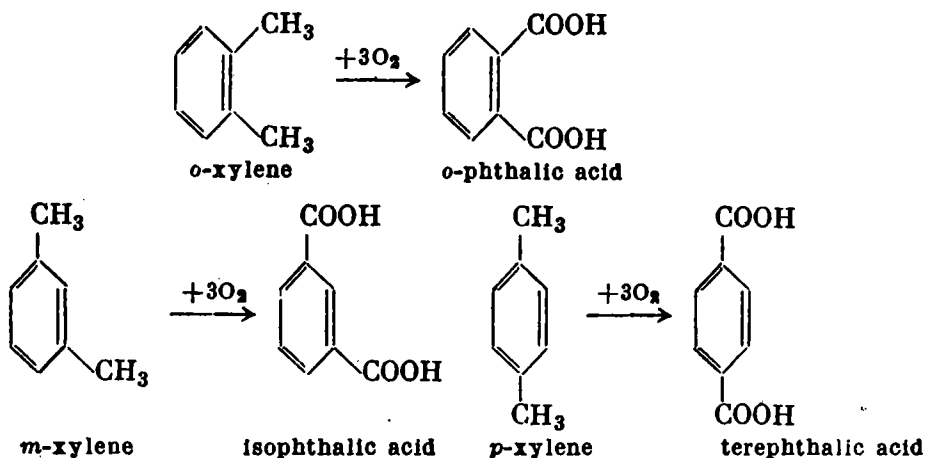
The saccharin tablets on sale consist of its sodium derivative:



This is known as *soluble saccharin* and is several times sweeter than sugar. Saccharin is not assimilated by the body in metabolism and is merely a sweetening agent.

237. Phthalic Acids. The oxidation of aromatic hydrocarbons whose molecules contain two side chains produces acids with two

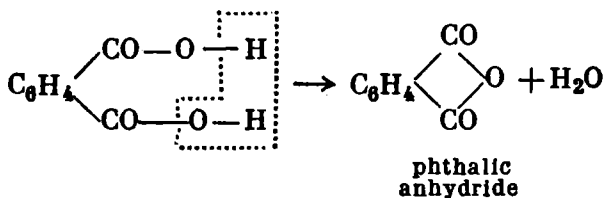
carboxyl groups, which are called *phthalic acids*:



The phthalic acids are solid crystalline substances.

The most important of the three is *o*-phthalic acid, which is often called simply phthalic acid. Large quantities of it are used in the synthesis of dyes and plastics. Industrially *o*-phthalic acid is manufactured by oxidizing naphthalene by concentrated sulphuric acid in the presence of mercuric sulphate (p. 485) or by the oxygen of the air in the presence of vanadium oxides as catalysts.

When heated above its melting point, *o*-phthalic acid loses water readily to become *phthalic anhydride*:

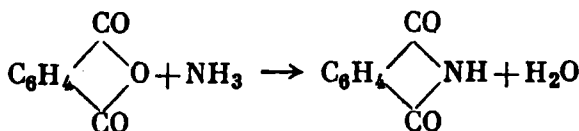


The two other isomers do not yield anhydrides.

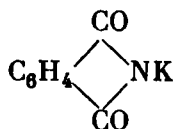
This difference in the behaviour of the phthalic acids is easily accounted for: in the *o*-phthalic acid molecule the carboxyls are closest to each other, which makes it possible for a five-membered cyclic anhydride to be formed with the loss of water.

Phthalic anhydride crystallizes in the form of bright needles of prisms; it melts at 130.8° , boils at 285° , and is easily sublimed.

When dry ammonia is passed through heated phthalic anhydride, an imide of phthalic acid, known as *phthalimide*, is formed:



Phthalimide crystallizes in the form of white leaflets (m.p. 238°). When phthalimide is treated with alcoholic potassium hydroxide, the hydrogen of the imide group is replaced by potassium. The product is potassium phthalimide:



The phthalic acids are important commercially.

Ortho-phthalic acid (in the form of phthalic anhydride) is produced industrially by the oxidation of naphthalene or *o*-xylene by the oxygen of the air over a catalyst of vanadium pentoxide. The diesters of *o*-phthalic acid (dimethylphthalate, dibutylphthalate, dioctylphthalate and others) have many uses.

Dimethylphthalate is a liquid, which boils at 282° and has a faint odour. It is used as a repellent to keep off mosquitoes.

Dibutylphthalate (a liquid, which boils at 340°) and *dioctylphthalate* (a liquid, which boils above 350°) are used as plasticizers for plastics.

The condensation of phthalic anhydride with polyhydroxy alcohols produces important synthetic resins (p. 438). Phthalic anhydride is an intermediate product in the manufacture of certain synthetic dyes.

Terephthalic acid, which is being produced in ever greater amounts, is the initial material in the manufacture of polyester fibres.

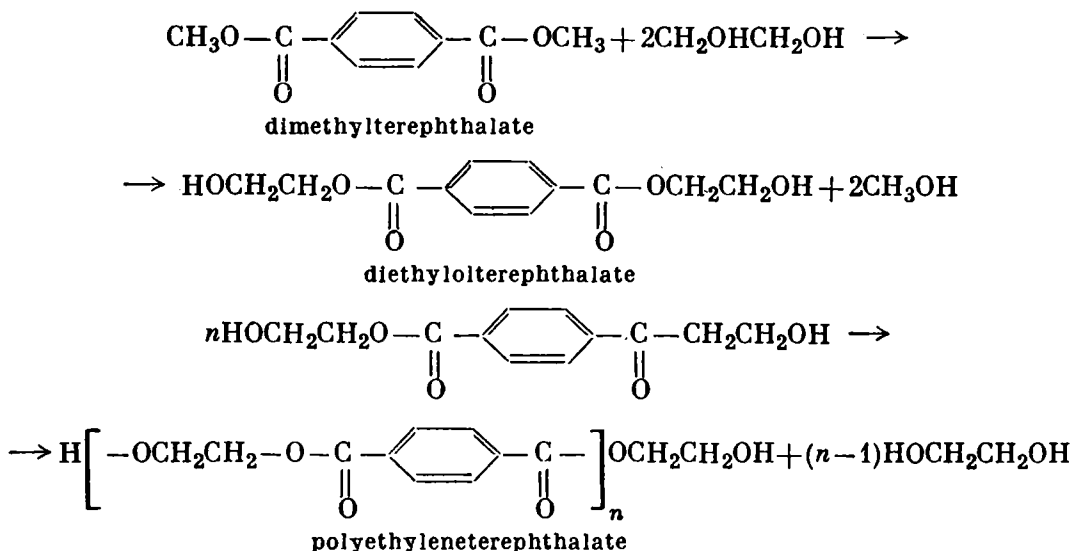
Isophthalic acid has little commercial importance. Its esters are used as plasticizers.

238. Polyester Resins. The polycondensation of dicarboxylic acids (adipic, maleic, phthalic, terephthalic, etc.) with polyhydroxy alcohols (ethylene glycol, glycerol, etc.) produces polyesters, many of which have come to be very important in the manufacture of synthetic fibres, plastics, protective coatings, and other synthetic materials.

Resins Based on Terephthalic Acid and Ethylene Glycol. The polycondensation of terephthalic acid and ethylene glycol produces the fibre-forming resin polyethyleneterephthalate, which has found extensive application in the manufacture of valuable polyester fibres.

In view of the difficulty of producing terephthalic acid of the required high degree of purity, the material used in industrial processes is ordinarily not the free acid, but its dimethyl ester, dimethylterephthalate. The re-esterification of that ester is accom-

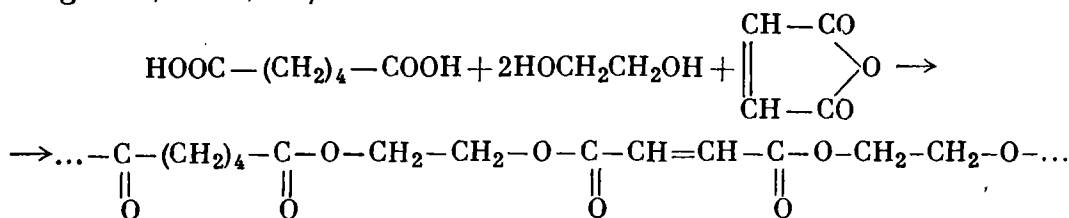
plished with ethylene glycol:



The polyester fibre based on polyethyleneterephthalate is called *lavsan** in the Soviet Union, *terylene* in Great Britain, and *dacron* in the United States. It has a high tensile strength and water resistance.

Especially widespread are textiles woven of a mixture of natural fibres (wool, cotton) and lavsan, since the addition of 30-50% of lavsan, while in no way detracting from the other qualities of the material, adds to it such valuable properties as great strength and wrinkle-resistance.

Unsaturated Polyesters. When a mixture of saturated and unsaturated dicarboxylic acids is esterified with glycols, the products are low-molecular liquid polyesters of linear structure (molecular weight 1,000-3,000):



At increased temperature and in the presence of polymerization initiators, these liquid polyester resins can copolymerize with other unsaturated compounds, such as styrene, forming polymers of a retic-

* The name lavsan is a contraction of the Russian for Laboratory of High-Molecular Compounds of the Academy of Sciences.

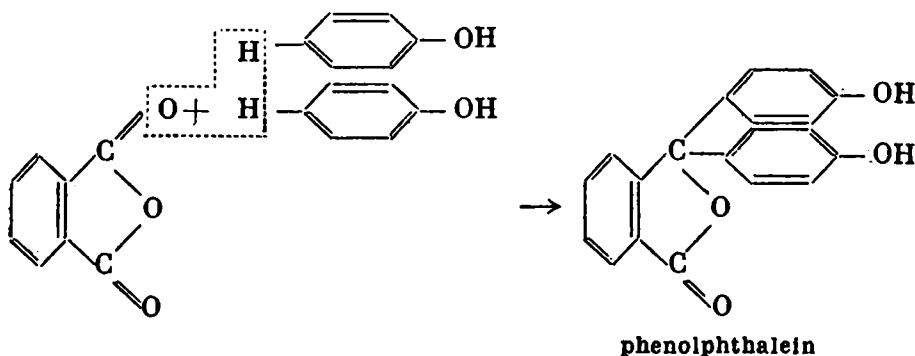
A low-molecular fusible resin is formed at first; it contains the reactive groups OH and COOH. With prolonged heating (150-180°), the resin is converted to an infusible solid state.

Pure glycerol-phthalic resins are not used because they form a very brittle film, which is affected by water. Fatty and resin acids are usually added to them, and this produces resilient oil-soluble resins with a high immunity to water.

Glyptals have many uses as electric insulating material and as varnishes immune to corrosion and weatherproof.

239. Phthaleins. Phthalic anhydride, when treated with dehydrating agents, is capable of condensing with phenols. This produces substances known as *phthaleins*. The simplest of the phthaleins is phenolphthalein.

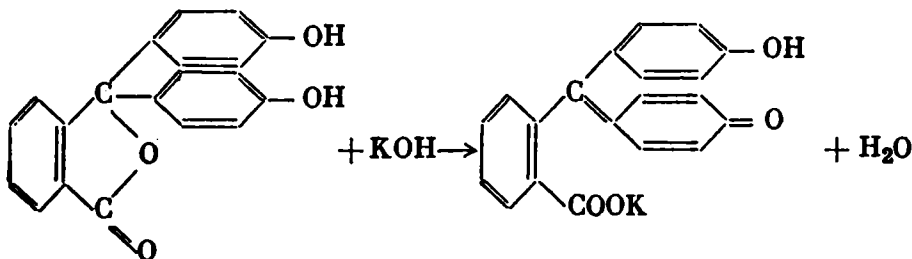
Phenolphthalein is prepared by heating a mixture of phthalic anhydride and phenol with sulphuric acid:



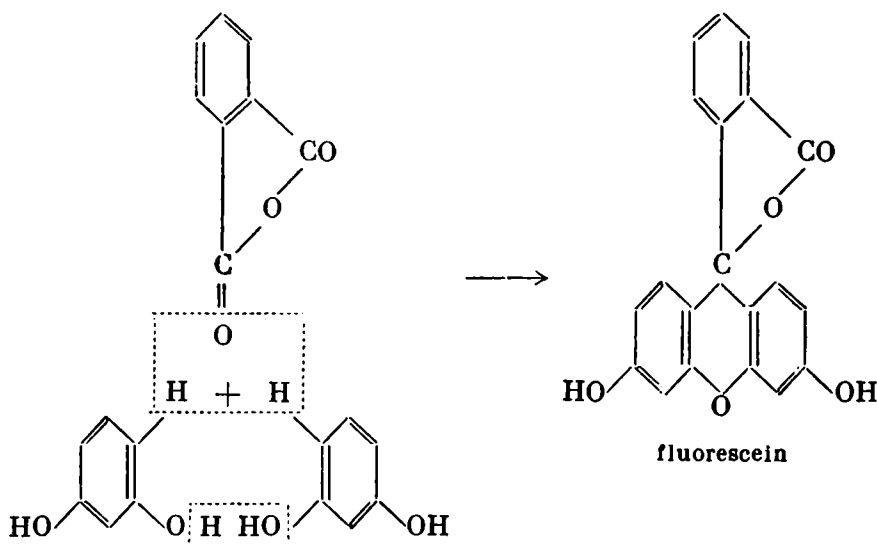
Phenolphthalein is a colourless solid, which dissolves in alkalis to form salts of a bright red colour.

It is used as an indicator in analysis and as a laxative medicinally.

The change in colour when phenolphthalein reacts with an alkali is due to the formation of the quinoid structure:



Another phthalein is *fluorescein*. This is prepared by fusing a mixture of phthalic anhydride and resorcin with zinc chloride:

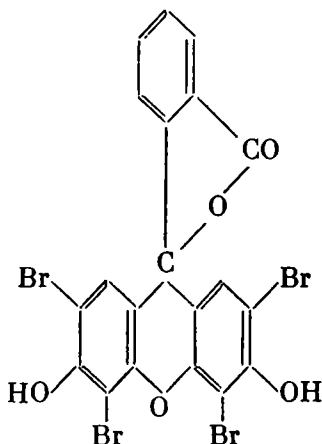


Fluorescein dissolves in alkalis, imparting a yellow colour and a yellowish green fluorescence to the liquid. The fluorescence is clearly evident even when the ratio of fluorescein to water is 1 : 40,000,000. For this reason fluorescein has been used to trace the flow of ground water.

Fibres of animal origin become bright yellow when treated with fluorescein.

The derivatives of fluorescein in which halogens and other substituents have taken the place of hydrogen atoms have valuable dyeing properties.

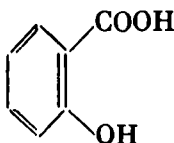
The simplest of these derivatives is tetrabromofluorescein, or *eosin* (from the Greek word *eos* meaning dawn):



Eosin gives silk a beautiful yellowish rose colour, with a splendid fluorescence. Various eosin preparations are used in microscopic research in biology and medicine.

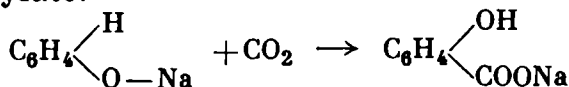
HYDROXYBENZOIC ACIDS

240. Salicylic Acid. Salicylic acid is both an acid and a phenol. The hydroxyl and the carboxyl in its molecule are in *o*-position to each other:

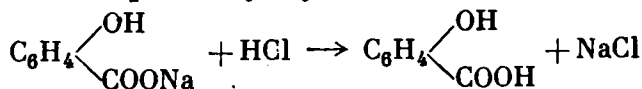


Another name for it is therefore *o*-hydroxybenzoic acid. Its derivatives occur in certain plants, for example, in the leaves and the bark of the willow. It is from the Latin name of the willow (*Salix*) that salicylic acid derives its name.

Industrially salicylic acid is made by heating sodium phenolate with carbon dioxide to 130° under pressure in autoclaves. The product is sodium salicylate:

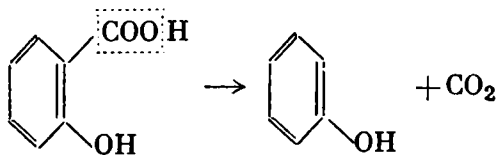


The salt is decomposed by hydrochloric acid:

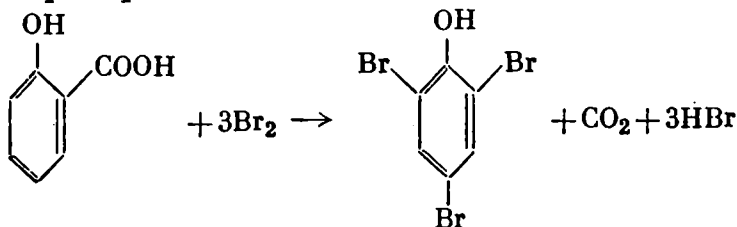


Salicylic acid is a crystalline substance with a low solubility in cold water; it melts at 159°. Like any phenol, it gives a violet colour with ferric chloride.

When heated quickly, it loses CO₂ and becomes phenol:

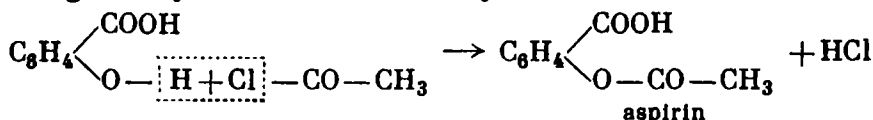


When a salicylic acid solution is treated with bromine water, bromine is substituted for the carboxyl and white 2,4,6-tribromophenol is precipitated:



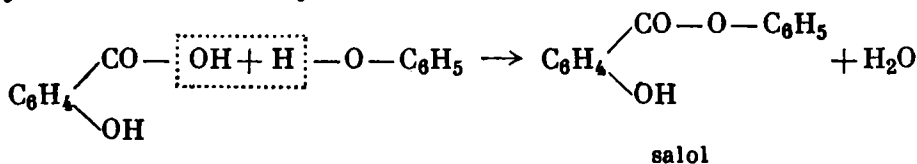
With alcohols and phenols, as well as with acids, salicylic acid forms esters.

The ester of salicylic acid (phenol group) and acetic acid—acetyl-salicylic acid—is commonly known as *aspirin*. It can be prepared by treating salicylic acid with acetyl chloride:



Aspirin (m.p. 135°) is widely used medicinally as an antipyretic.

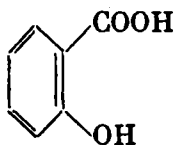
The ester of salicylic acid (carboxyl group) and phenol—phenyl salicylate—is commonly known as *salol*:



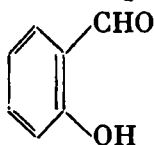
Salol is prepared by heating a mixture of sodium salicylate with phosphorus trichloride and phenol; the intermediate product is therefore salicylic acid chloride.

Salol (m.p. 43°) is an intestinal antiseptic. It passes through the stomach (where there is normally an acid medium) unchanged, but is hydrolyzed in the intestines, where the medium is alkaline.

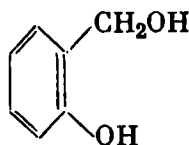
Salicylic acid prevents fermentation and putrefaction: it is therefore used as a preservative for food (caviare) and beverages (beer). It is also used as a semi-product in the manufacture of many dyes. An aldehyde and an alcohol correspond to the acid:



salicylic acid

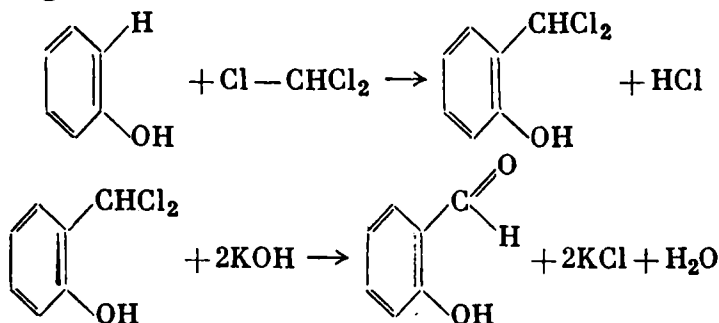


salicylaldehyde



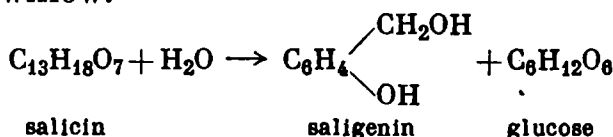
salicyl alcohol

Salicylaldehyde is a liquid (b.p. 197°) with a pleasant odour. It can be prepared by the *Reimer-Tiemann synthesis*, which consists in heating phenols with chloroform and potassium hydroxide. This is a two-stage reaction:



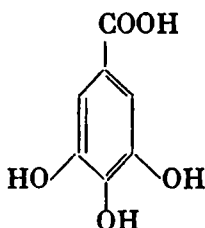
The aldehyde group in this case assumes an *o*- or *p*-position in relation to the hydroxyl, the *o*-isomer forming the bulk of the product.

Salicyl alcohol, or *saligenin*, is a crystalline substance. It is formed by the hydrolysis of *salicin* $C_{13}H_{18}O_7$, a glucoside contained in the bark of the willow:



Saligenin is also produced, by the action of formaldehyde upon phenol, as an intermediate in the manufacture of phenolformaldehyde resins.

241. Gallic Acid. Another important hydroxybenzoic acid is gallic acid:

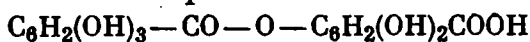


In the free state it occurs in oak-galls, tea leaves, and oak bark; considerable amounts of gallic acid are contained in the form of esters and glucosides in tanning matter of the tannin type. The acid crystallizes with one molecule of water, forming silky needles. Upon heating, it loses CO_2 and forms pyrogallol (p. 425).

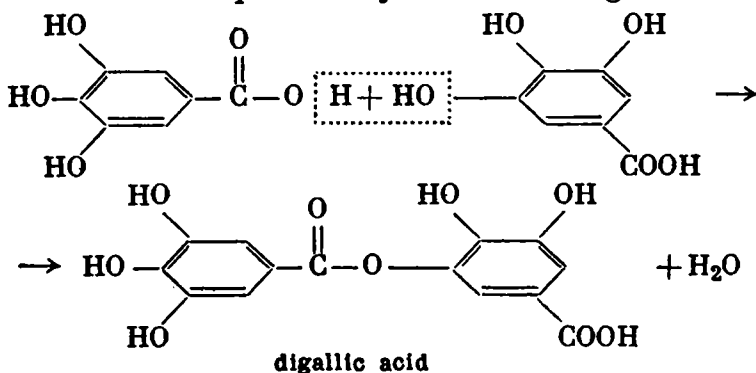
With a solution of ferric salts the acid produces a black liquid, the iron ink used formerly. With glue it forms a compound insoluble in water; this accounts for the action of tanning matter, used in leather manufacture. A solution of gallic acid has a sour, astringent taste.

Hydroxybenzoic acid molecules can react with one another to form esters.

Digallic acid is an example of such an ester:



Its formation can be expressed by the following reaction:



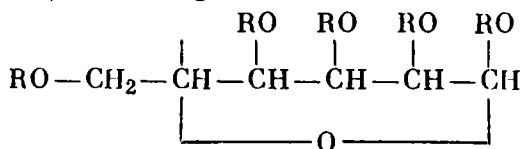
This is called *m*-digallic acid because the esterified hydroxyl is in *m*-position in relation to the carboxyl.

Hydroxybenzoic acid esters similar to digallic acid have been called *depsides* (from the Greek word *depsis* which means tanning); they are closely related to certain tanning agents.

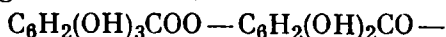
242. Tanning Matter. The tanning agents are compounds of astringent taste, which form dark blue and dark green precipitates with ferric chloride; they precipitate proteins and turn animal hides into leather. They are readily soluble in water.

Tanning matter is contained in many plants, e.g., in willow and oak bark; especially rich in tanning matter are certain tropical plants: the catechu, the Turkish nut-gall dividivi, the acacia, and the Colorado quebracho.

A typical tanning agent is *tannin*, which can be obtained most readily from nut-galls. These are excrescences on the leaves and branches of the oak, caused by the injurious effect on the plant of the gall wasp. Tannin is contained in tea and is responsible for its bitter taste; it is a white powder that dissolves readily in water. When boiled with hydrochloric acid, it is converted completely into gallic acid and glucose. Chinese tannin is an ester of glucose (oxide modification) and digallic acid:



where R is the digallic acid residue



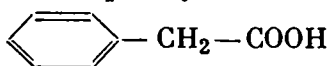
Tannins from different plants have a different composition. In the tannins derived from some plants the digallic acid residues have been partly replaced by gallic acid residues.

Tannin serves as mordant in dyeing and as an astringent in medicine.

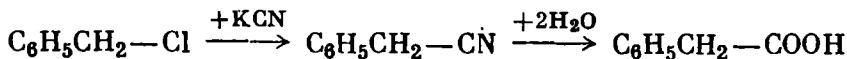
Structurally tanning agents are closely related to the hydroxybenzoic acids. They are divided into two classes. The members of one class readily undergo hydrolysis, breaking up into simpler compounds; their behaviour is that of esters. The members of the other class, when fused with alkalis, yield various hydroxybenzoic acids and phenols, chiefly pyrocatechol and phloroglucinol.

ACIDS WITH A SIDE-CHAIN CARBOXYL

243. Phenylacetic Acid. In the acids described above the carboxyl is linked directly to the benzene ring. The simplest acid with a carboxyl in the side chain is phenylacetic acid:

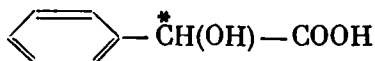


It is easily prepared from benzyl chloride:

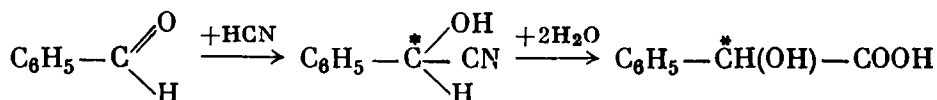


Phenylacetic acid melts at 76.9° and boils at 266.5° . Its ethyl ester is used in scents.

244. Phenoxyacetic Acid. Phenoxyacetic acid has the formula:

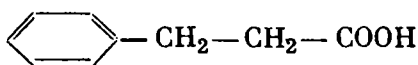


Its molecule has an asymmetric carbon atom; accordingly, it exists in the form of optical antipodes. The acid can be prepared from benzaldehyde and hydrocyanic acid:



Phenoxyacetic acid melts at 118° .

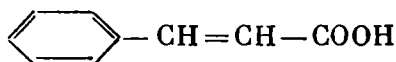
245. β -Phenylpropionic Acid. Beta-phenylpropionic, or hydrocinnamic, acid



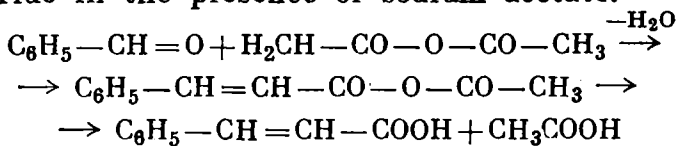
can be prepared by reducing cinnamic acid, e.g., by means of sodium amalgam. It melts at 48.6° and boils at 280° .

Beta-phenylpropionic acid and its *p*-hydroxy derivative have a direct bearing upon certain products of protein hydrolysis.

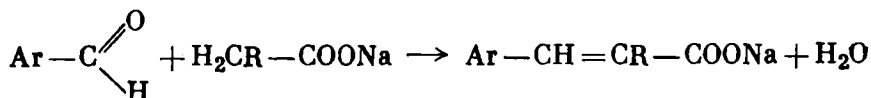
246. Cinnamic Acid. Cinnamic acid



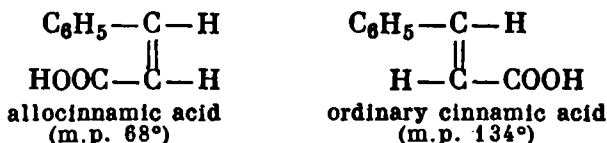
serves as an example of the aromatic acids with a double bond in the side chain. It is prepared by heating benzaldehyde with acetic anhydride in the presence of sodium acetate:



The heating of aromatic aldehydes with the sodium salts of fatty acids in the presence of the anhydrides of those acids is a general method of preparing aromatic acids with a carboxyl in an unsaturated side chain. This is called the *Perkin reaction*. If we denote the aromatic radical as Ar and the aliphatic radical as R, we can write the reaction in general form as follows:



Cinnamic acid exhibits *cis-trans* isomerism:

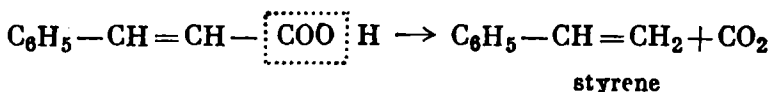


Ordinary cinnamic acid occurs in the balsams of certain plants (Peru balsam, Tolu balsam), mostly tropical. The balsams, in addition to resinous substances, chiefly contain the esters of cinnamic and benzoic acids with benzyl and cinnamic alcohols.

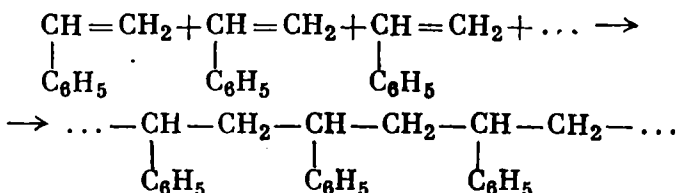
The cinnamic acid esters are used in scents.

Cinnamic acid has all the properties of unsaturated compounds: it readily adds bromine or hydrogen bromide, is oxidized by potassium permanganate, etc.

Slow distillation causes the acid to lose CO_2 , yielding the hydrocarbon *styrene*:

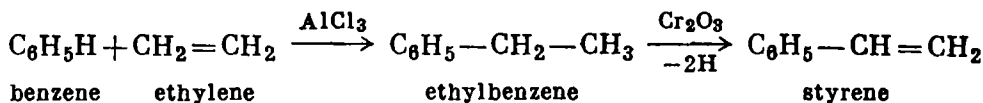


Styrene is a liquid with a pleasant odour, which boils at 145°. It polymerizes readily, forming high-molecular polymers of $(\text{C}_8\text{H}_8)_n$ composition, known as *polystyrenes*. Polymerization proceeds slowly even at ordinary temperature; heating accelerates it considerably. Styrene polymerization follows this pattern:



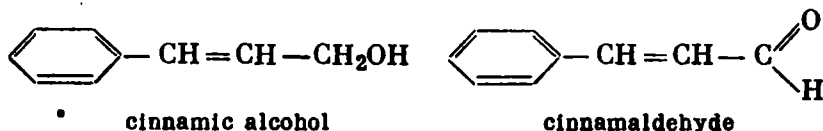
It produces a glassy mass, which is used for insulation in electrical engineering, for making chemically resistant ware and apparatus, type, etc. When polystyrene is heated to 300°, it is depolymerized back to styrene.

Polystyrene plastics have proved very valuable and are produced in enormous quantities. The styrene is prepared from benzene and ethylene (petroleum cracking gases), which are treated with anhydrous aluminium trichloride. The resulting ethylbenzene is dehydrogenated over a catalyst (Cr_2O_3) at 400°:



The copolymerization of styrene and butadiene produces valuable types of synthetic rubber.

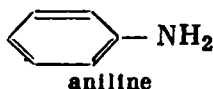
An alcohol and an aldehyde correspond to cinnamic acid:



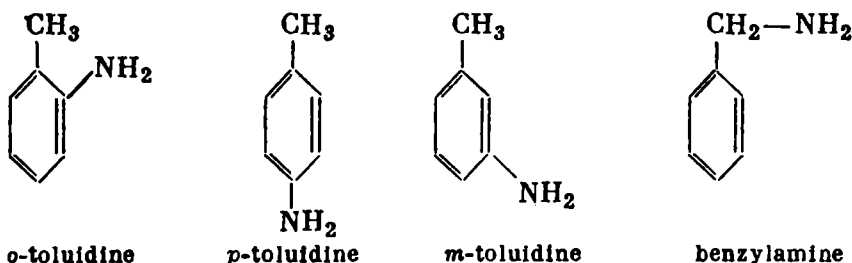
Cinnamic alcohol is a solid (m.p. 33°; b.p. 257°) with an odour of hyacinth. *Cinnamaldehyde* is a liquid boiling at 251° with partial decomposition. It is the fragrant substance of cinnamon.

AROMATIC AMINES

247. Preparation and Properties of Primary Aromatic Amines. The simplest aromatic amine is phenylamine or aminobenzene, $C_6H_5-NH_2$, known as *aniline*:



The closest homologue of aniline, the amine derivative of toluene, is known in the form of four isomers. Three of them contain an amino group linked to the benzene ring; they are called *toluidines*. The fourth has the amino group in the side chain; it is called *benzylamine*

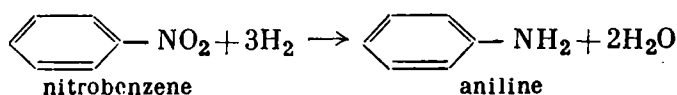


Amines containing the amino group in the side chain are in chemical properties similar to the aliphatic amines. We shall therefore confine ourselves to considering amines containing the amino group attached directly to the benzene ring.

Primary aromatic amines are prepared by one reaction only, which was discovered in 1842 by the famous Russian chemist N. Zinin*. He carried out the first synthesis of aniline (and, by the

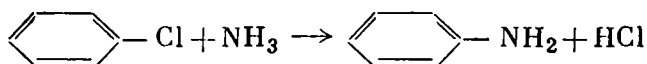
* Nikolai Zinin (1812-80) was born in the town of Shusha, in the Transcaucasus. In 1830 he entered the Physics and Mathematics Department of Kazan University. His dissertation (1836) was entitled: "Concerning the Phenomena of Chemical Affinity and the Superiority of Berzelius's Theory of Constant Chemical Proportions to Berthelot's Static Chemical Concept". His D.Sc. dissertation at St. Petersburg University in 1841 had the title: "Concerning the Benzoyl Compounds and Some Newly-Discovered Bodies Belonging to the Benzoyl Series".

same method, of α -naphthylamine and *m*-phenylenediamine) by reducing a nitrogen compound:



Zinin's reducing agent was a solution of ammonium sulphite. Nowadays nitrogen compounds are usually reduced by metals (Fe, Sn, Zn) in an acid medium or by leading nitrobenzene vapour with hydrogen over a catalyst (Cu) at 300-400°.

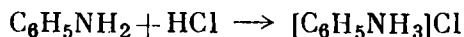
Aliphatic amines are prepared by the action of ammonia upon alkyl halides. The preparation of aromatic amines by such a procedure is scarcely feasible: the halogen is firmly attached to the benzene ring and does not react readily with ammonia. The heating of chlorobenzene with ammonia under a high pressure does yield aniline:



Aromatic amines have the following properties:

1. The primary aromatic amines are liquids with a high boiling point or solids; they have a specific odour and are slightly soluble in water.

2. Aliphatic amines have pronounced basic properties: they form salts with acids and their aqueous solutions are markedly alkaline. Aromatic amines, on the other hand, are weak bases: their aqueous solutions do not turn litmus blue, although with acids these amines do form salts. The reaction of aniline with hydrochloric acid thus produces anilinium chloride:



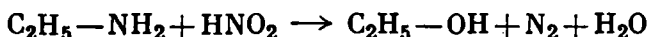
This salt is usually called aniline hydrochloride, and its composition is represented by the formula $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$.

On his return to Kazan, where he was given the Chair in Chemical Technology, Zinin turned to a new field of organic compounds. As early as October 1842 the Academy of Sciences' bulletin (*Izvestia Akademii Nauk*) printed his paper on the conversion of nitrobenzene and nitronaphthalene into "benzoidam" (aniline) and "naphthilidam" (naphthylamine) by the action of hydrogen sulphide in an ammoniacal medium.

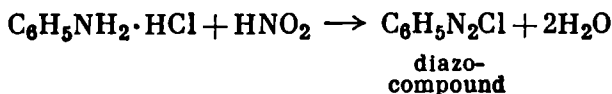
Zinin's laboratory in Kazan produced several superb papers on the synthesis of reduction products of mono- and dinitrogen compounds of the aromatic division. The compounds synthesized included azoxybenzene, hydrazo-benzene, benzidine, and *m*-nitroaniline. The significance of these papers was summed up aptly by A. W. Hofmann at a meeting of the German Chemical Society. "Even if Zinin had done nothing except convert nitrobenzene to aniline", Hofmann said, "his name would still be inscribed in the annals of chemistry in gigantic letters".

The basic properties of the amino group in aromatic amines are thus weakened. This is the effect of the benzene residue, the phenyl radical, which enhances acidic properties.

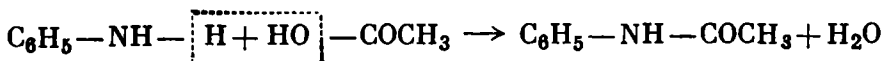
3. The treatment of primary aliphatic amines with nitrous acid produces alcohols:



But when the salts of primary aromatic amines are treated with nitrous acid, they are not converted to hydroxyl derivatives at once; at first they form the industrially highly important *diazo-compounds* (p. 462. fol.):

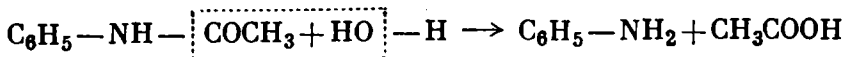


4. When primary aromatic amines are treated either with acids (with prolonged heating) or with their anhydrides (in the cold state), *anilides* are formed. For example, the reaction of aniline and acetic acid yields acetanilide:



It is evident from its formula that acetanilide is a derivative of aniline, in whose molecule one atom of hydrogen has been replaced by the acyl radical. It can also be regarded as a derivative of acetic acid, in whose molecule a hydroxyl has been replaced by an aniline residue.

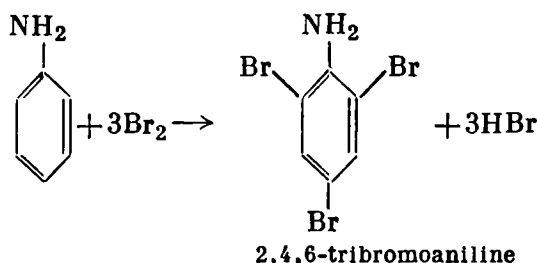
When boiled with acids or alkalis, the anilides add water and break up again into an amine and an acid:



5. The benzene ring in aromatic amines in the main retains its properties: a halogen can be substituted for hydrogen, and aromatic amines can be sulphonated and nitrated.

The substitution of a halogen for hydrogen in the ring of amines, as of phenols, takes place more readily than in aromatic hydrocarbons. It will be remembered that the $-\text{NH}_2$ group has a strong first-class orienting effect (p. 406 fol.). The treatment of aniline with bromine water, accordingly, gives rise to tribromoaniline, in which the bromine atoms are in *o*- and *p*-positions in relation to the amino

group:



6. Aromatic amines undergo oxidation readily.

248. Aniline and Its Derivatives. Aniline is a colourless oily liquid, which is heavier than water and boils at 184.4° . It is only slightly soluble in water (100 g of water dissolves 3.2 g of aniline).

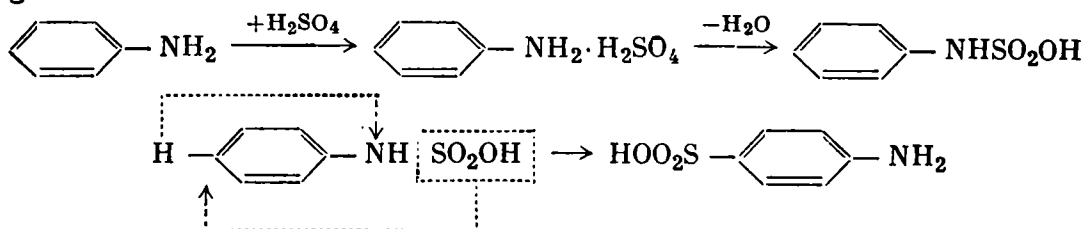
Aniline is oxidized quite easily and undergoes a change of colour in the process. When treated with bleaching powder, for instance, it turns violet. If aniline is dissolved in strong sulphuric acid and potassium dichromate is added, a green colour appears, which subsequently turns to blue and, finally, to black.

The dye formed by the oxidation of aniline by potassium dichromate is called *aniline black*. In dyeing fabrics black with aniline, the fabrics are covered with aniline hydrochloride (aniline salt) and then treated with a solution containing potassium dichromate, sulphuric acid, and other substances; in conclusion they are subjected to special treatment called ageing.

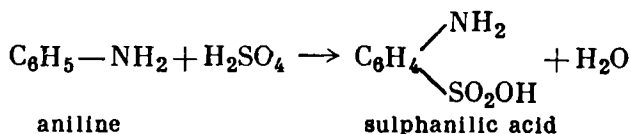
Aniline salts, such as aniline hydrochloride or aniline sulphate, turn wood yellow. The more inferior the grade of paper, i.e., the more wood it contains and the less pure cellulose, the more pronounced its colouring by aniline.

Aniline is one of the basic products of the chemical industry. It is used extensively in the preparation of dyes, medicinals, and substances which accelerate the vulcanization of rubber and the synthesis of many organic compounds.

Sulphanilic Acid. The sulphonation of aniline is not difficult to accomplish. It can be brought about by heating aniline with concentrated sulphuric acid to $180\text{--}190^\circ$. This produces aniline-*p*-sulphonic acid, known as *sulphanilic acid*. At first sulphuric acid is added to aniline, and a salt is formed; this loses water, yielding an anilide; finally, the sulphoxyl changes places with the *p*-hydrogen atom:



The over-all reaction can be expressed by the following equation:



Sulphanilic acid crystallizes in the form of glistening plates, which have the composition $\text{C}_6\text{H}_4(\text{NH}_2)\text{SO}_2\text{OH} \cdot 2\text{H}_2\text{O}$ and are but slightly soluble in cold water; the crystals experience weathering when exposed to air.

Sulphanilic acid exhibits pronounced acidic properties and reacts with alkalis and soda to form soluble salts. It does not form salts with acids.

Sulphanilic acid is something in the nature of an "inner" salt: salt formation takes place through the interaction of the basic amino group with the acidic sulfoxyl within the same molecule:

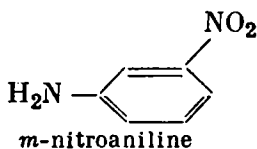
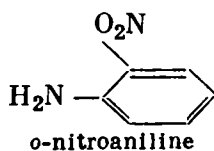


The formation of the inner salt is due to the low solubility of the acid in water (although, as a rule, the aromatic sulphonic acids are highly soluble).

Sulphanilic acid is used in the synthesis of many dyes.

A very important part in modern medicine is played by the derivatives of its amide, the sulpha drugs (p. 469-70).

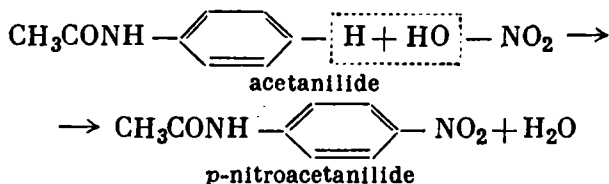
Nitroanilines. The nitroanilines contain both the nitro group and the amino group:



The nitroanilines are crystalline substances. The *p*- and *m*-isomers are yellow; *o*-nitroaniline is orange-yellow.

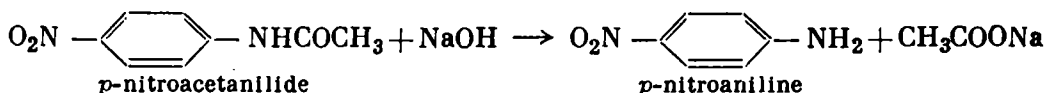
The preparation of nitroanilines by nitrating aniline is somewhat difficult, owing to the fact that nitric acid not only nitrates the aniline, but also partly oxidizes it. To prepare *p*-nitroaniline the aniline is therefore first converted to acetanilide $\text{C}_6\text{H}_5\text{—NH—COCH}_3$ (or the anilide of acetic acid), which is oxidized less readily than aniline; this, in effect, protects the amino group from oxidation.

The acetanilide is nitrated, with the result that the nitro group assumes a *p*-position with relation to the amino group:



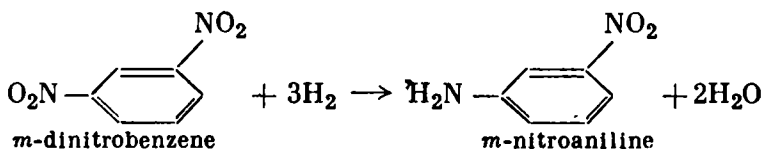
The saponification of *p*-nitroacetanilide by an alkali yields *p*-nitroaniline, which is a most important material in dye manufacture.

The process of saponification may be expressed as follows:

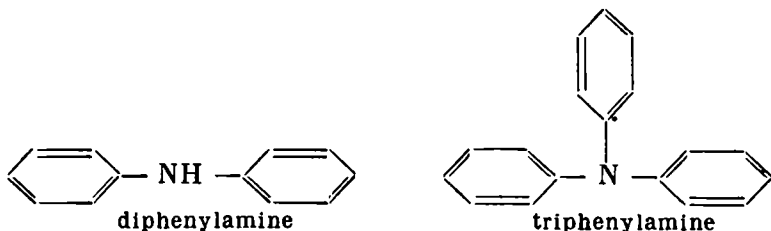


A small amount of *o*-nitroaniline is also formed in nitration, with the *p*-nitroaniline.

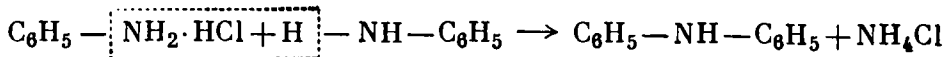
Meta-nitroaniline is prepared by partially reducing* the readily available *m*-dinitrobenzene:



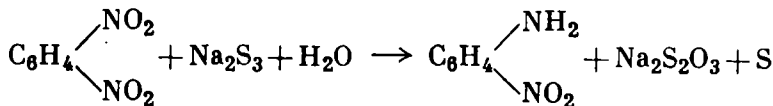
249. Secondary and Tertiary Amines. Aniline contains the NH_2 amino group and is therefore a primary amine. There are also secondary and tertiary aromatic amines, such as the crystalline compounds diphenylamine $(\text{C}_6\text{H}_5)_2\text{NH}$ and triphenylamine $(\text{C}_6\text{H}_5)_3\text{N}$:



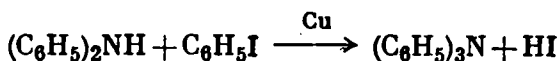
Diphenylamine can be prepared by heating aniline hydrochloride and free aniline in an autoclave to 200-220°:



* The reduction of a single nitro group is achieved by heating the dinitrogen compound with sulphides or polysulphides of alkali metals or of ammonia:



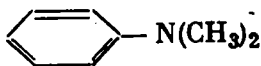
Triphenylamine can be obtained by boiling diphenylamine with iodobenzene, potassium carbonate, and copper powder:



Diphenylamine has even weaker basic properties than aniline, and its salts are easily decomposed by water. Triphenylamine exhibits practically no basic properties. The accumulation of phenyl groups in this way attenuates basic properties.

A solution of diphenylamine in concentrated sulphuric acid is a sensitive reagent for nitric acid. Even traces of nitric acid, when added to this solution, produce a bright blue colour. The reaction can, however, be used to detect nitric acid only in the absence of other oxidizing agents, since diphenylamine likewise gives a blue colour with bromine water, potassium permanganate, hydrogen peroxide, etc. Diphenylamine serves as an intermediate in the synthesis of certain dyes; in addition to this, it is also used as a stabilizer for smokeless gunpowders. Nitrocellulose, which forms the bulk of smokeless gunpowder, is prone to decompose spontaneously. This spontaneous decomposition, which gradually gains momentum, can cause the whole mass of gunpowder to explode. An 0.5-1.5% addition of diphenylamine—or of certain other substances, for that matter—prevents the nitrocellulose in smokeless gunpowders from decomposing.

Dimethylaniline



is an example of a mixed aromatic-aliphatic amine. It is prepared by heating a mixture of aniline hydrochloride and methanol in an autoclave:

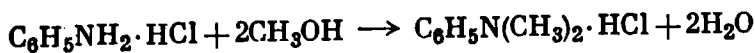


Fig. 67 shows an installation used to prepare dimethylaniline. Dimethylaniline is an oily colourless liquid with a specific odour. Like the other aromatic-aliphatic amines, it has more pronounced

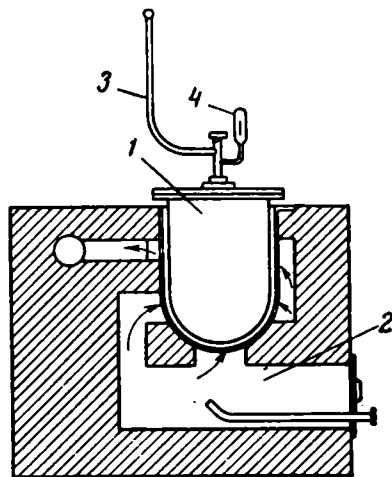
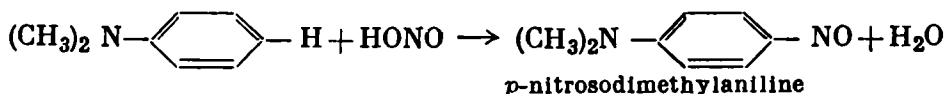


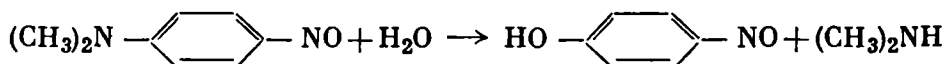
Fig. 67. Installation for preparing dimethylaniline:

1—autoclave; 2—furnace; 3—outlet; 4—pressure gauge.

basic properties than purely aromatic secondary and tertiary amines. The hydrogen atom in *p*-position to the $-\text{N}(\text{CH}_3)_2$ group is extremely mobile; when dimethylaniline is treated with a weak solution of nitrous acid, it is replaced by the nitrosyl group with the formation of *p*-nitrosodimethylaniline:

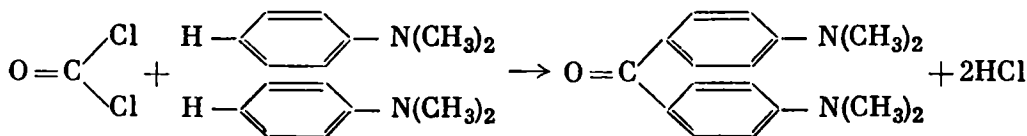


The green crystals of *p*-nitrosodimethylaniline melt at 85° . When the compound is boiled with alkalis, it decomposes to *p*-nitrosophenol (white needles) and dimethylamine:



This reaction serves to prepare dimethylamine without admixtures of methylamine or trimethylamine.

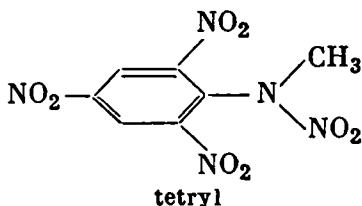
The high mobility of the hydrogen atom in *p*-position is also borne out by other reactions of dimethylaniline, e.g., its reaction with phosgene, which yields Michler's ketone:



Michler's ketone can be regarded as benzophenone in whose molecule the hydrogen atoms of both benzene rings in *p*-positions to the carbonyl have been replaced by $-\text{N}(\text{CH}_3)_2$ groups. It may also be called *di-(p*-dimethylamino) benzophenone.

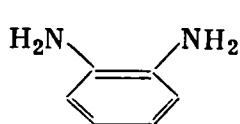
Michler's ketone (colourless crystals) is used in the synthesis of certain dyes.

When dimethylaniline is nitrated by nitric acid, three nitrogen groups are substituted for hydrogen atoms of the ring, while a fourth takes the place of one of the methyl groups. The resulting compound is *tetryl*, or trinitrophenylmethylnitramine:

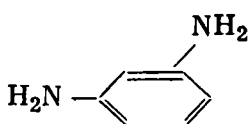
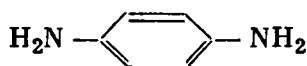


Tetryl (pale yellow crystals which melt at 130°) is one of the most powerful explosives.

250. Diamines. The simplest aromatic diamines are the diamino derivatives of benzene, called *phenylenediamines*:



o-phenylenediamine

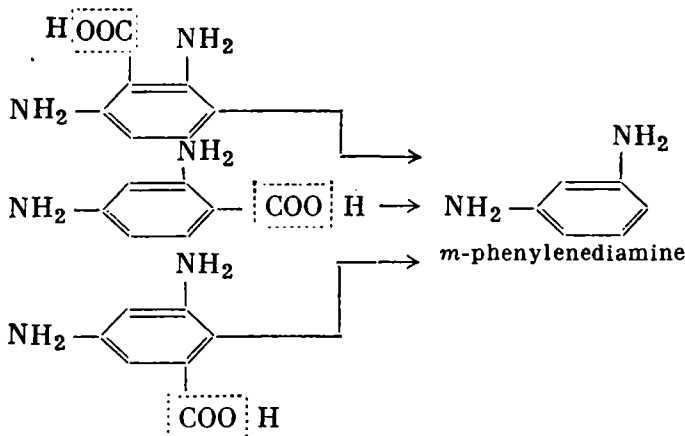
*m*-phenylenediamine*p*-phenylenediamine

Ortho-phenylenediamine and *p*-phenylenediamine are prepared by reducing the corresponding nitroanilines; *m*-phenylenediamine, by reducing *m*-dinitrobenzene.

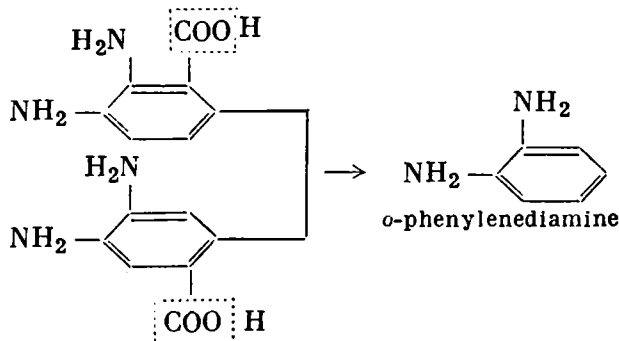
The phenylenediamines are crystalline substances, which dissolve very readily in hot water. They are easily oxidized and turn dark upon exposure to air. The phenylenediamines are weak bases. They form salts with two acid equivalents. Meta-phenylenediamine and para-phenylenediamine are used in synthesizing dyes.

Whether a disubstituted benzene derivative has an *o*-, *m*-, or *p*-structure can be determined by the number of isomers that can be derived from it when a third hydrogen atom of the benzene ring is replaced by some other atom or radical. Six diaminobenzoic acids are known, corresponding to the formula $C_6H_3(NH_2)_2COOH$. The acids give up CO_2 to form phenylenediamines.

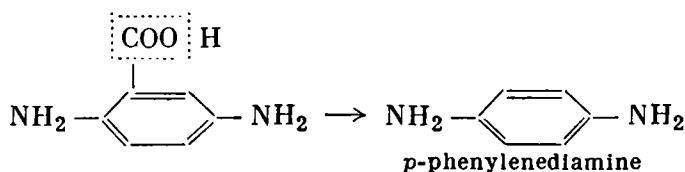
Meta-phenylenediamine (b.p. 284°) can be prepared from three diaminobenzoic acids:



Ortho-phenylenediamine (b.p. 257°) can be prepared from two diaminobenzoic acids:



Para-phenylenediamine (b. p. 267°) can be prepared from only one diaminobenzoic acid:



Consequently, in the case of disubstituted compounds with two identical substituents three tri-substituted isomers correspond to the *m*-structure, two tri-substituted isomers, to the *o*-structure, and one tri-substituted isomer, to the *p*-structure.

The physical properties of the aromatic amines are given in Table 20.

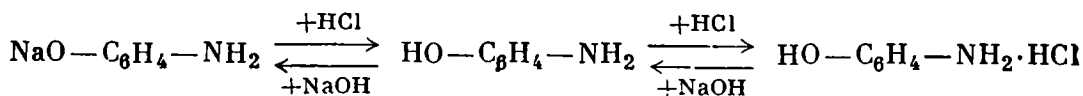
TABLE 20. Physical Properties of Aromatic Amines

Amine	Formula	M.p., °C	B.p., °C	Solubility in g per 100 g water
Aniline	C ₆ H ₅ NH ₂	−6	184.4	3.5 at 25°
<i>o</i> -Toluidine	CH ₃ C ₆ H ₄ NH ₂	−24.4	200.3	1.5 at 25°
<i>m</i> -Toluidine	CH ₃ C ₆ H ₄ NH ₂	−31.2	203.4	slightly soluble
<i>p</i> -Toluidine	CH ₃ C ₆ H ₄ NH ₂	44	200.5	0.730 at 21°
Dimethylaniline	C ₆ H ₅ N(CH ₃) ₂	2.4	194	very slightly soluble
Diphenylamine	(C ₆ H ₅) ₂ NH	53.5	302	insoluble
Triphenylamine	(C ₆ H ₅) ₃ N	127	365	"
<i>o</i> -Phenylenediamine	C ₆ H ₄ (NH ₂) ₂	102	257	{ dissolve very readily in hot water
<i>m</i> -Phenylenediamine	C ₆ H ₄ (NH ₂) ₂	62.8	284	
<i>p</i> -Phenylenediamine	C ₆ H ₄ (NH ₂) ₂	139.7	267	

AMINOPHENOLS AND AMINOBENZOIC ACIDS

251. Aminophenols. *Aminophenols are substances that are both aromatic amines and phenols.*

They are solid crystalline substances. Ortho-aminophenol melts at 172°; *p*-aminophenol, at 186°, and *m*-aminophenol, at 122°. Since they are amines and phenols at the same time, the aminophenols form salts both with acids and with alkalis:



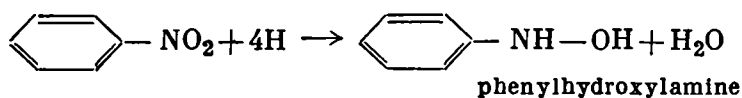
The salts dissolve in water more readily than do the aminophenols themselves. Aqueous, and especially alkaline, solutions of the aminophenols are easily oxidized by the oxygen of the air. As strong reducing agents, the aminophenols, like hydroquinone and pyrogallol, are used in photography in the role of developers. Development is essentially the reduction of silver halides to metallic silver. The process is, however, too complicated to be represented here by an equation. It will merely be pointed out that the benzene ring of an organic developer must contain no less than two OH groups or an OH group and a NH_2 group in *o*- or *p*-position. In the initial stage of oxidation two hydrogen atoms are detached from these groups.

The formulas and names of several photographic developers are given in Table 21.

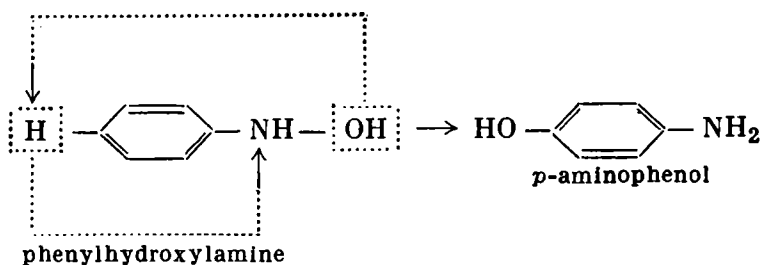
TABLE 21. Photographic Developers

Chemical name	Formula	Name as developer
Para-aminophenol hydrochloride	$\text{HO}-\text{C}_6\text{H}_4-\text{NH}_2\cdot\text{HCl}$	rodinal
Para-methylaminophenol sulphate	$\text{HO}-\text{C}_6\text{H}_4-\text{NH}(\text{CH}_3)\cdot\text{H}_2\text{SO}_4$	metol
2,4-Diaminophenol hydrochloride	$\text{HO}-\text{C}_6\text{H}_3(\text{NH}_2)_2\cdot\text{HCl}$	amidol
Hydroquinone	$\text{C}_6\text{H}_4(\text{OH})_2$	hydroquinone
Pyrogallol	$\text{C}_6\text{H}_3(\text{OH})_3$	pyro

Para-aminophenol is manufactured chiefly by the electrolytic reduction of nitrobenzene. This is accomplished by subjecting to electrolysis a solution of sulphuric acid with nitrobenzene in it in the suspended state. The hydrogen evolved at the cathode reduces the nitrobenzene to *phenylhydroxylamine*:

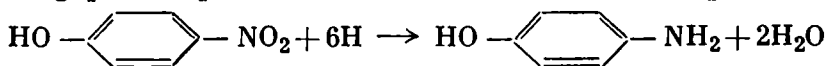


Phenylhydroxylamine $\text{C}_6\text{H}_5\text{NH-OH}$ can be looked upon as a derivative of hydroxylamine $\text{NH}_2\text{-OH}$, in whose molecule a hydrogen atom attached to the nitrogen has been replaced by a phenyl. In an acid solution phenylhydroxylamine undergoes a rearrangement and turns into *p*-aminophenol:



In this reaction the hydroxyl and the hydrogen atom in *p*-position change places.

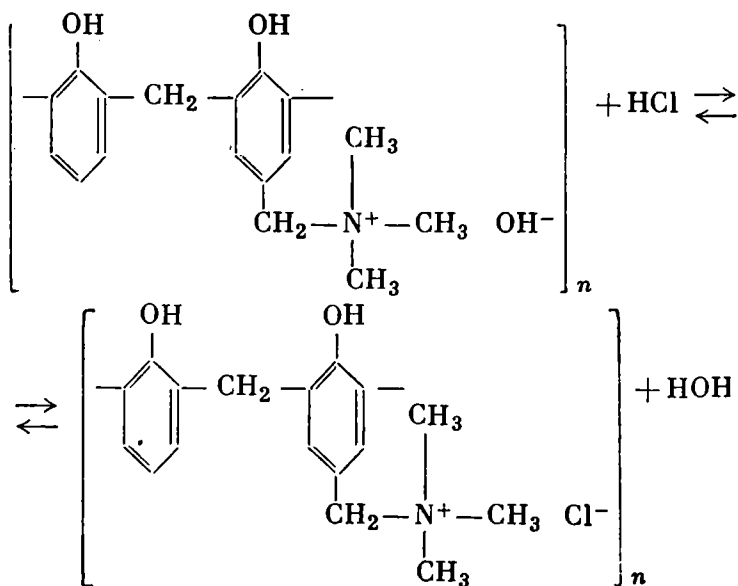
Para-aminophenol can also be prepared by another method: by reducing *p*-nitrophenol. The reaction can be represented thus:



252. Ion Exchange Resins. Like phenol, the aromatic diamines, aminophenols, and amines readily undergo polycondensation with formaldehyde. Provided the components are in the required proportion and the pH suitable, the products are high-molecular compounds of a reticular spatial structure. Usually these are black or dark brown glass-like substances, which are insoluble in water or other solvents. In water and aqueous solutions of salts and acids they tend to swell.

When they swell in water, these substances form an insoluble macromolecular cation and an OH^- -ion. They do so because they contain $-\text{NH}-$ or $-\text{NH}_2$ polar groups of a basic character. These substances can therefore be regarded as high-molecular weak bases.

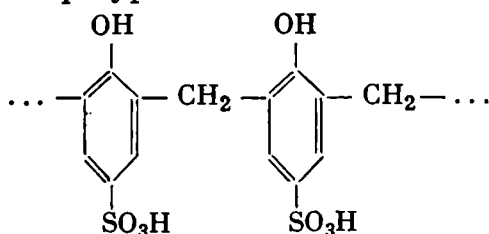
It is a distinctive feature of these polymers that they undergo a reaction of double decomposition with electrolyte solutions, forming salts:



The swelling of the polymer base in aqueous solutions of salts increases the speed of ion diffusion in the polymer. This in turn accelerates the reaction of ion exchange and involves all the available basic groups of the polymer in the reaction, despite the insolubility of the polymer. By treating the resulting salt with water, it is possible to obtain the initial compound again.

The ability of such polymers to undergo reversible reactions with electrolytes makes it possible to use these polymers as ion exchange filters for extracting anions from solutions. Accordingly, high-molecular bases have come to be known as *anion exchange resins*, or *anionites*.

The condensation of *n*-phenol-sulphonic acid with formaldehyde yields sulphonated polyphenols:



These are high-molecular acids that are insoluble, but swell in water. These polymers readily absorb cations from aqueous solutions of salts.

By treating the polymer salts with acids it is possible to isolate the salts of metals in the pure state. High-molecular compounds containing the acidic ionic groups $-\text{OH}$, $-\text{SO}_3\text{H}$, or $-\text{COOH}$ are called *cation exchange resins*, or *cationites*.

Ion exchange resins have extensive industrial uses. They have made it possible to separate chemically similar compounds, such as mixtures of amino acids or alkaloids. Besides, they have facilitated the selective extraction of acids or bases from solutions of their mixtures.

Large numbers of various synthetic ion exchange resins are now produced industrially (for example, the multi-purpose cationites KU-1 and KU-2, or the weakly-basic anionites AN-1 and AN-2).

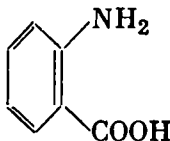
Anionites and cationites are usually characterized by their exchange capacity (mostly in mg-eq/ml). This capacity is the greater, the more ion exchange groups (amino, hydroxyl, sulpho, or carboxyl respectively) the resin contains.

The resin particles have a porous structure. For the proper selection of an ion exchange resin, it is necessary to know its density, swelling capacity, and its statistical and complete exchange capacities.

It has been noted that cations are best displaced by hydrogen ions and anions by hydroxyl ions. Accordingly, to prepare the hydrogen

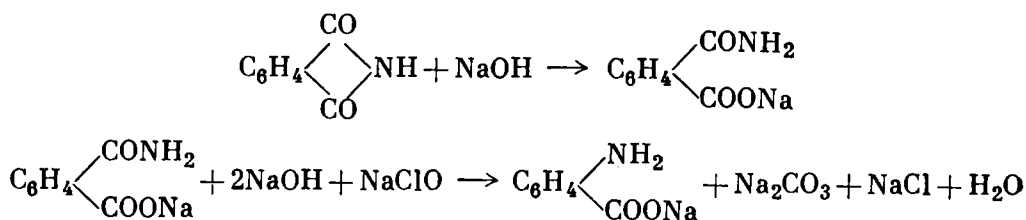
form of a cationite it is treated with dilute HCl. Anionites are used in the form of bases containing the OH group. They are prepared by treating the resin with dilute NaOH.

253. Aminobenzoic Acids. Of the three theoretically possible aminobenzoic acids the most important is *o*-aminobenzoic acid, or *anthranilic acid*:

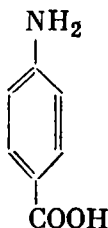


Anthranilic acid melts at 145° , has a sweet taste, and dissolves readily in water and in alcohol. It is used to make certain dyes (indigo) and medicinals; its methyl ester is used in scents.

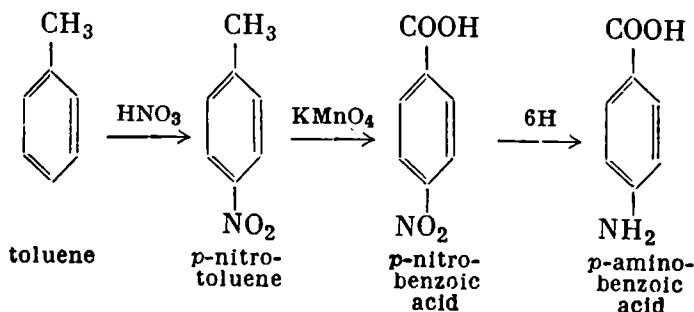
Industrially anthranilic acid is manufactured by treating phthalimide with an alkali and hypochlorates. A salt of phthalamic acid is formed at first, but this then undergoes a Hofmann rearrangement (p. 335) to a salt of anthranilic acid:



Para-aminobenzoic acid

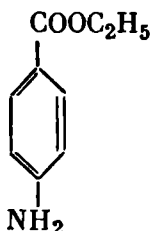


(colourless crystals) melts at $187\text{--}188^{\circ}$. It is prepared from toluene by means of the following process:

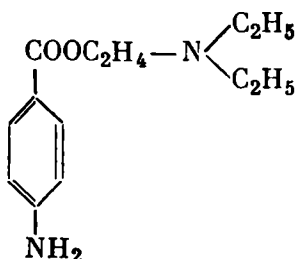


Para-aminobenzoic acid is the initial material for synthesizing a number of local anaesthetics, including:

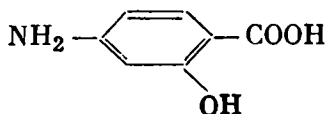
anaesthesine (ethyl *p*-aminobenzoate)



and *procaine* (diethylaminoethyl *p*-aminobenzoate):

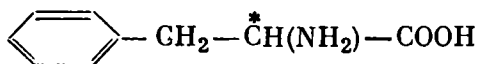


Another derivative of *p*-aminobenzoic acid is *p*-aminosalicylic acid (PAS)



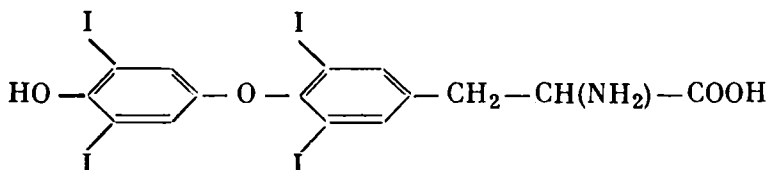
It is used in the treatment of tuberculosis.

254. Phenylalanine. Phenylalanine



can be regarded as a derivative of alanine (p. 345), in whose molecule the hydrogen atom attached to the β -carbon atom has been replaced by a phenyl radical.

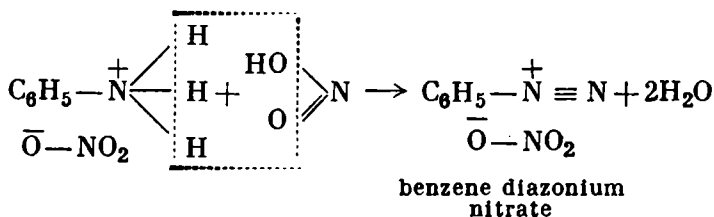
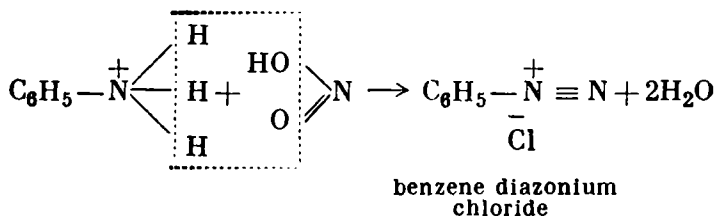
Laevorotatory phenylalanine (m.p. 280°) and *p*-hydroxyphenylalanine, or *tyrosine*, $\text{HO}-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$ (m.p. $316-320^\circ$) are formed in the hydrolysis of nearly all proteins. A very important derivative of tyrosine is *thyroxine*:



Thyroxine (m.p. 321°) was isolated in 1919 from the thyroid gland. It is a hormone regulating the metabolic rate. Its structure was established in 1926 by the study of its decomposition products and by synthesis.

DIAZO-COMPOUNDS

255. Preparation and Structure of Diazo-Compounds. Diazo-compounds are prepared by the action of nitrous acid on the salts of primary aromatic amines.* Aniline hydrochloride, for instance, yields a substance of the composition $C_6H_5N_2Cl$, which is called benzene diazonium chloride, while the nitrate of the same amine yields benzene diazonium nitrate $C_6H_5N_2NO_3$:



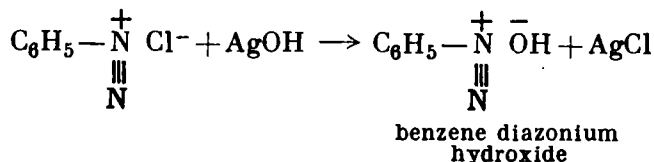
The diazo-compounds, as is evident from these equations, can be regarded as derivatives of ammonium salts, in which an aromatic radical has been substituted for one hydrogen atom, and a nitrogen atom, for three others. Such an ammonium derivative is called *diazonium*.

The diazo-compounds, like the ammonium salts, are salt-forming substances, which in aqueous solution are almost completely dissociated into $C_6H_5\overset{+}{N}_2$ and Cl^- ions and which are absolutely neutral, notwithstanding the fact that one of the ions is an acid radical.

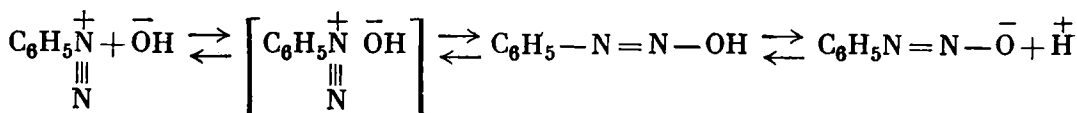
If a solution of benzene diazonium chloride is treated with moist silver oxide, a curdy precipitate of silver chloride is formed, while the solution becomes strongly alkaline. The very unstable benzene diazonium hydroxide formed is a base as strong as the caustic alka-

* The reaction is conducted by adding to the amine salt a mineral acid and an equivalent amount of sodium nitrite. The action of the acid on the sodium nitrite produces nitrous acid, which then reacts with the amine salt.

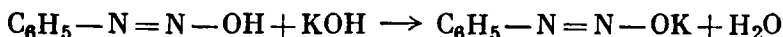
lis (NaOH and KOH):



The solution, however, rapidly loses its alkaline properties. This is due to the conversion of the hydroxide to its isomer, *diazohydroxide*, which exhibits the properties of a weak acid:



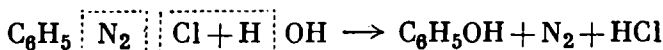
The action of alkalis speeds this conversion and results in the formation of diazotates, diazo-hydroxide salts:



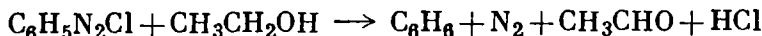
Excess mineral acid reconverts the diazotates to diazonium salts.

The diazonium salts are highly unstable; many of them are explosive in the dry state*; they are easily decomposed and are capable of a variety of reactions. With the aid of diazonium salts it is possible to prepare a wide range of most diverse substances. Some of the reactions of the diazo-compounds are accompanied by the evolution of free nitrogen; others are not.

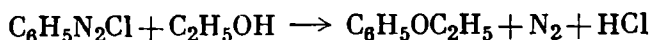
256. Diazo-Compound Reactions with Nitrogen Evolution. 1. When solutions of diazonium salts in water are heated, the acid radical breaks away, the $-\overset{+}{\text{N}}\equiv\text{N}$ group is replaced by a hydroxyl, and phenols are formed:



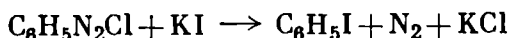
2. When diazo-compounds are heated with alcohols, two parallel reactions take place, one of them in some cases being preponderant. In one of the reactions a molecule of alcohol gives up two hydrogen atoms, which convert the diazo-compound to an aromatic hydrocarbon, while the alcohol is oxidized to an aldehyde:



The second reaction results in ethers:

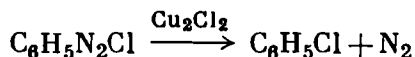


3. The heating of diazo-compound solutions with potassium iodide leads to iodine substitution in the ring:

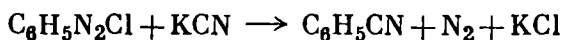


* For this reason it is customary to work with aqueous solutions of diazonium salts.

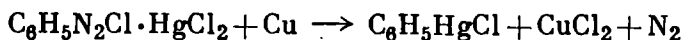
4. When solutions of diazonium chloride or bromide are heated in the presence of a corresponding cuprous halide (or copper powder), nitrogen is evolved and the halogen takes the place of the diazo-group:



5. The treatment of diazonium salts in certain conditions with potassium cyanide produces nitriles. Thus, the action of potassium cyanide on benzene diazonium chloride yields benzonitrile:



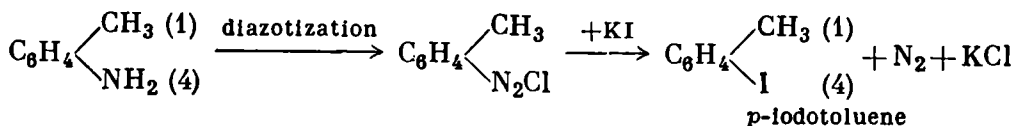
6. With mercuric chloride diazo-compounds form double salts, which, as shown by Nesmeyanov, decompose in the presence of copper powder to form organomercury compounds:



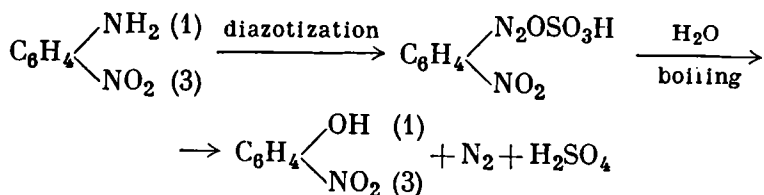
Aromatic derivatives of antimony and lead can be obtained similarly (A. Nesmeyanov, K. Kocheshkov, and O. Reutov).

257. Syntheses Involving Diazo-Compounds. The readily available aromatic amines can be used for synthesizing, via diazo-compounds, many benzene derivatives that cannot be prepared by direct reactions. Examples of such syntheses are given below.

Synthesis of p-Iodotoluene. Para-toluidine serves as the initial material for the synthesis:

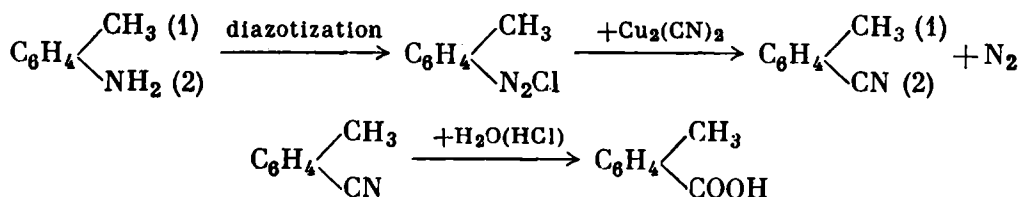


Synthesis of m-Nitrophenol. The direct nitration of phenol does not yield *m*-nitrophenol, but it can be prepared through a diazo-compound from readily available *m*-nitroaniline:

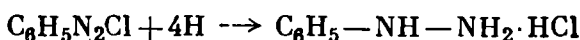


Synthesis of o-Toluic Acid. The initial material is *o*-toluidine, which is usually obtained from *o*-nitrotoluene. The diazotization of *o*-toluidine yields *o*-tolyl diazonium chloride. When this is treated with cuprous cyanide $\text{Cu}_2(\text{CN})_2$ in a potassium cyanide solution, the diazo-compound is decomposed and a nitrile is formed. The latter can be hydrolyzed by heating with hydrochloric acid

or sulphuric acid:



258. Reduction of Diazo-Compounds. Hydrazines. Reduction converts diazo-compounds to derivatives of hydrazine $\text{NH}_2\text{—NH}_2$. For example, the reduction of benzene diazonium chloride produces phenylhydrazine hydrochloride:

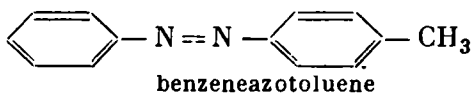
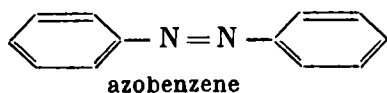


Phenylhydrazine crystallizes in the form of plates (m.p. 23° ; b.p. 241°), readily undergoes oxidation, becomes brown upon exposure to air, and has basic properties. It is used in investigating aldehydes, ketones, and sugars (because of the formation of phenylhydrazones and osazones). It is also used to synthesize many substances that have extensive applications, e.g., antipyrine, pyramidon, and certain dyes.

Some of the other reactions of the diazo-compounds, not accompanied by the evolution of nitrogen, are described in the section on azo-dyes.

AZO-COMPOUNDS AND AZO-DYES

259. Azo-Compounds. *The azo-compounds are compounds whose molecules contain the —N=N— azo-group, the free valencies of this group being linked to hydrocarbon radicals.* Two examples of such substances are azobenzene and benzeneazotoluene:

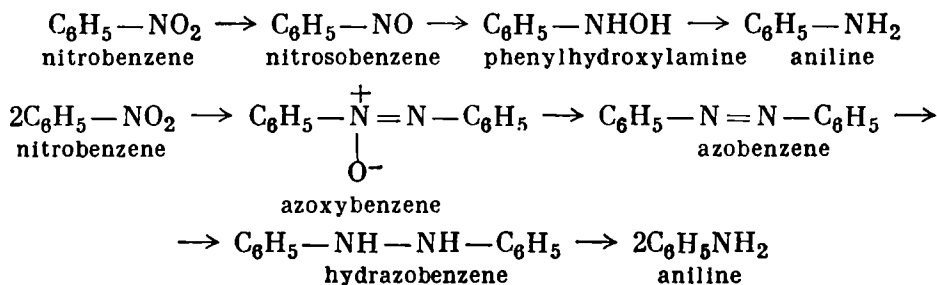


Azo-compounds are prepared by reducing nitrogen compounds. Azobenzene, for instance, can be prepared by reducing nitrobenzene by tin chloride in the presence of excess potassium hydroxide.

The end products of the reduction of nitrogen compounds are amines.

Intermediate reduction products are, however, known in the aromatic division; they can be prepared either by reducing nitrogen compounds in properly chosen conditions or, sometimes, by oxidiz-

ing amines. They can be arranged in two series:

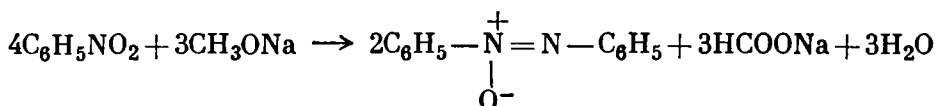


The molecules of the substances in one series contain a single nitrogen atom, while the molecules of the substances in the other series contain two nitrogen atoms. The substances of the second series are prepared by reducing nitrogen compounds in an alkaline medium.

Phenylhydroxylamine $\text{C}_6\text{H}_5-\text{NHOH}$ can be prepared by reducing nitrobenzene by zinc dust in a solution of ammonium chloride. It crystallizes in the form of colourless needles (m.p. 81°). For the rearrangement of phenylhydroxylamine to *p*-aminophenol see p. 457.

Nitrosobenzene $\text{C}_6\text{H}_5-\text{NO}$ is prepared by oxidizing phenylhydroxylamine by chromic acid mixture. It crystallizes in the form of colourless needles (m.p. 68°). In the molten state and in solution it is bluish green. In the solid state nitrosobenzene is dimolecular. When melted or dissolved, it dissociates and acquires the colour of the monomolecular form.

Azoxybenzene $\text{C}_6\text{H}_5-\overset{+}{\underset{\text{O}^-}{\text{N}}}=\text{N}-\text{C}_6\text{H}_5$ is usually prepared by boiling nitrobenzene with sodium methyrate, which is oxidized to sodium formate:



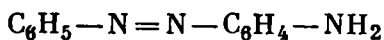
Azoxybenzene crystallizes in the form of pale yellow needles (m.p. 36°). When distilled with iron filings, it is reduced to *azobenzene*.

Hydrazobenzene $\text{C}_6\text{H}_5-\text{NH}-\text{NH}-\text{C}_6\text{H}_5$ is prepared by reducing nitrobenzene or azobenzene by zinc dust and potassium hydroxide. Hydrazobenzene (colourless crystals) melts at 131° . Strong reducing agents convert it to aniline; the oxygen of the air oxidizes it easily, reconverting it to azobenzene. For the benzidine rearrangement see p. 475 fol.

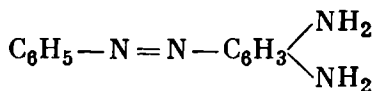
The azo-compounds are the most important of the intermediate reduction products of the nitrogen compounds. The simplest non-substituted azo-compounds are either red or orange. Azobenzene, for instance, is an orange-red crystalline substance melting at 68° . Although coloured, the azo-compounds are not, however, dyes. This is because they are not retained by fabrics.

260. Aminoazo-Compounds and Hydroxyazo-Compounds. The amino derivatives of the azo-compounds are called aminoazo-compounds.

Two examples are:

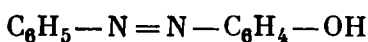


aminoazobenzene

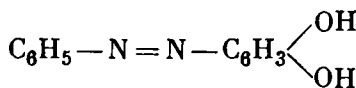


diaminoazobenzene

The hydroxy derivatives of the azo-compounds are called hydroxyazo-compounds. The following are two examples of these substances:

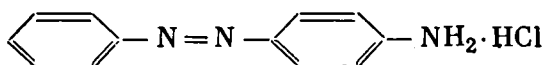


hydroxyazobenzene

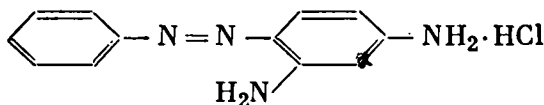


dihydroxyazobenzene

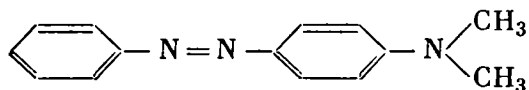
As can be seen from these formulas, the aminoazo-compounds contain an amino group; for this reason they are capable of forming salts with acids. The hydroxyazo-compounds contain a hydroxyl attached to the ring, i.e., are phenols, and are therefore capable of forming salts with alkalis. These salts are soluble in water. In the form of these salts the aminoazo-compounds and the hydroxyazo-compounds are used extensively as dyes. The dyes of this type are known as *azo-dyes*. The simplest dyes of this class are *p*-aminoazobenzene hydrochloride, also called *aniline yellow*



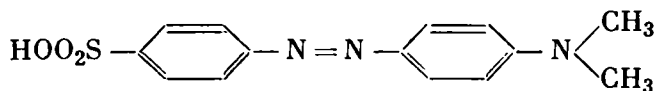
and 2,4-diaminoazobenzene hydrochloride, or *chrysoidine*



The more complex azo-dyes are compounds in which hydrocarbon radicals have taken the places of the hydrogen atoms of the amino group, e.g., *p*-dimethylaminoazobenzene



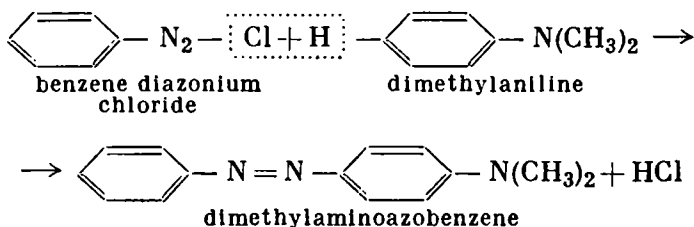
whose hydrochloride is a yellow dye. Some of these compounds contain a sulphoxyl, e.g., dimethylaminoazobenzene sulphonic acid



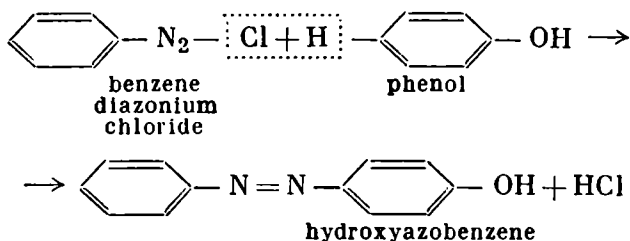
which is known as *helianthine*, or *methyl orange**.

* The indicator methyl orange used in analytical chemistry is the sodium salt of this sulphonic acid.

261. Preparation of Azo-Dyes. The aminoazo-compounds are prepared from diazo-compounds and aromatic amines. When a tertiary amine is treated with a diazonium chloride, the chlorine combines with a hydrogen atom of the amine's benzene ring, while the diazonium and amine residues form an aminoazo-compound:



Hydroxyazo-compounds are prepared by the reaction between diazonium salts and phenols:

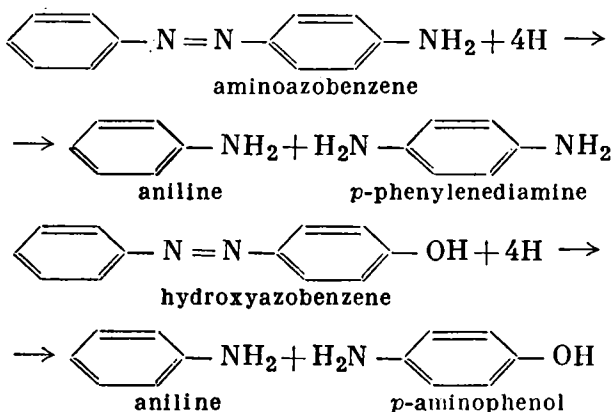


To reduce the acidity of the medium, these reactions are conducted in the presence of sodium hydroxide, soda, or sodium acetate. The sodium hydroxide and the soda neutralize the hydrochloric acid formed. The sodium acetate reacts with the hydrochloric acid to form sodium chloride and acetic acid. The addition of sodium acetate therefore replaces the strong hydrochloric acid in the solution with weak acetic acid.

This type of reaction, in which two components—a diazo-compound and an amine (or phenol)—interact to yield an azo-compound, is called a *coupling reaction*.

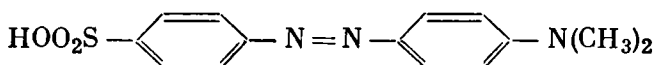
It is evident from the structural formulas of dimethylaminoazobenzene and hydroxyazobenzene that the amino group and the hydroxyl in their molecules are in *p*-position to the azo-group. This is a general rule: in the reactions of diazonium salts with phenols or amines, the replacement of the hydrogen in most cases takes place in *p*-position with respect to the hydroxyl or the amino group. If the *p*-position is occupied by some other group, the *o*-hydrogen is replaced.

Azo-dye structure is established by identifying the amines formed when the dyes are reduced. Reduction ruptures the bonds between the nitrogen atoms, and each of them forms an amino group:

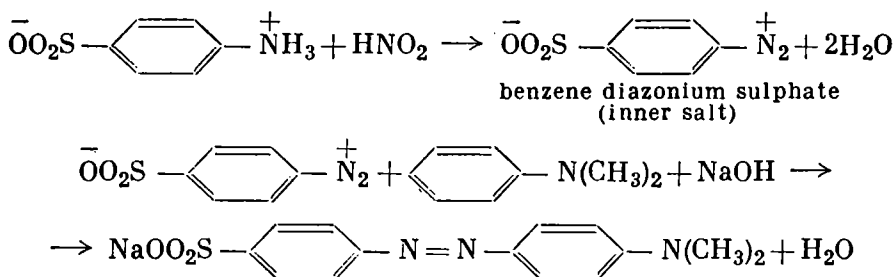


The azo-dyes are used chiefly for dyeing textile fibres, but some of them also have other uses. For example, helianthine (methyl orange) is used in analytical chemistry as an indicator. Prontosil (see below) has been used against streptococcal and staphylococcal infections.

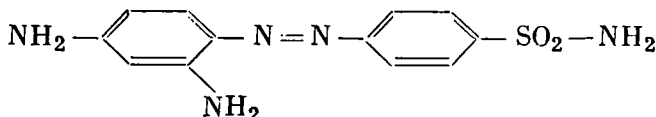
Helianthine, i.e., dimethylaminoazobenzene sulphonic acid,



is prepared by the diazotization of sulphanilic acid and the coupling of the resulting diazo-compound with dimethylaniline:



Prontosil has the structure:

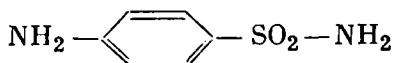


It is prepared by coupling the diazotized amide of sulphanilic acid with *m*-phenylenediamine.

Prontosil was the first potent means of combating diseases caused

by pathogenic cocci. Its anti-streptococcal action was discovered in experiments with white mice in 1935 by the bacteriologist Gerhard Domagk. In a short period of time the drug became highly widespread. It was administered in the treatment of streptococcal sore throat, childbed streptococcal fever, acute endocarditis, various erysipelatic cases, etc.

The sulphanilic acid amide



is known as *prontosil album*.

Domagk had for some years been studying the effect of various compounds, both described earlier and first synthesized by the chemists working with him, on streptococci. Although some of these compounds proved highly active, they were for various reasons unsuitable for treating streptococcal infections. Some, such as several compounds of gold, produced a general intoxication of the organism; others (some of the derivatives of quinine), while active locally, proved ineffective against general streptococcal infection, and still others exhibited activity only *in vitro*, i.e., in the test-tube, but not *in vivo*, i.e., in the living organism. Many azo-dyes had been known since 1913 to be active *in vitro*. Domagk was successful only when he turned his attention to azo-dyes containing the sulphonamide group SO_2NH_2 ; one of them was prontosil. Unlike the other azo-dyes, these substances are active only *in vivo*. The vehicle of anti-streptococcal activity in the azo-dyes is the sulphonamide group of atoms. The removal of this group makes the dyes inactive in the body. If, on the other hand, the group remains, the potency is preserved even when the rest of the molecule undergoes changes.

Shortly afterwards it was demonstrated that one of the products of the decomposition of prontosil in the organism was potent against streptococci. This was the amide of sulphanilic acid, which had been synthesized back in 1908.

This amide (prontosil album) is, like prontosil, used in treating erysipelas, acute sore throat and its complications, streptococcal meningitis, and other streptococcal diseases. Moreover, prontosil album is highly potent not only against general streptococcal infection, but also when applied locally to festering wounds and burns.

The discovery of the anti-streptococcal activity of this amide gave an impetus to the synthesis of new compounds containing the sulphonamide group; about 3,000 of these substances were synthesized in five years. They included sulphapyridine (p. 562) and sulphathiazole (p. 551), which are closely related to prontosil album.

262. Dyes and Dyeing. The aminoazo-compounds and the hydroxyazo-compounds, as pointed out above, are dyes. Dyes, or dye-stuffs, are substances capable of colouring fabrics in such a manner that the colour cannot be removed by rubbing or by washing. Dyes should be distinguished from coloured substances; azobenzene, for instance, is orange-red, but it is not a dye, i.e., it is not capable of colouring fibre.

The questions naturally arise: what causes the appearance of col-

our in a substance and what requirements must be met for a coloured substance to be a dye?

Some substances absorb light rays of all colours quite evenly. When a beam of white rays is passed through such a substance, they emerge merely attenuated in brightness, but still white. Such substances are colourless. Coloured substances, on the other hand, primarily absorb rays of definite colours, i.e., of definite wavelengths; they exhibit what is called selective absorption. When a beam of white rays is directed at such a substance (or its solution), the rays emerging from it (assuming that no phenomena other than light absorption take place) will no longer be white, but will be of the colour resulting from the mixing of all the colours of the spectrum except those absorbed. For example, if a substance absorbs blue-green rays, the emerging rays will be red, as red can be obtained by mixing all the other colours of the spectrum except the blue-green. Some substances are selective absorbers only in the infrared and the ultraviolet range. Benzene, for instance, exhibits selective absorption in the ultraviolet. Such to all intents and purposes colourless substances are, strictly speaking, likewise coloured. But ordinarily it is customary to regard as coloured only those substances that exhibit selective absorption in the visible range.

According to the *chromophore theory* of Witt, the colour of organic compounds may be traced to the presence in the molecule of special groups: chromophores and auxochromes.

The *chromophores* (colour-bearers) are groups capable of absorbing light of a definite wavelength. A characteristic structural feature of chromophores is the presence of unsaturated atoms and double bonds. The nitro group $-\text{NO}_2$, the nitrosyl group $-\text{N}=\text{O}$, and the azo-group $-\text{N}=\text{N}-$ are examples of strong chromophores.

A chromophore weaker in its effect is the carbonyl group $\text{>C}=\text{O}$.

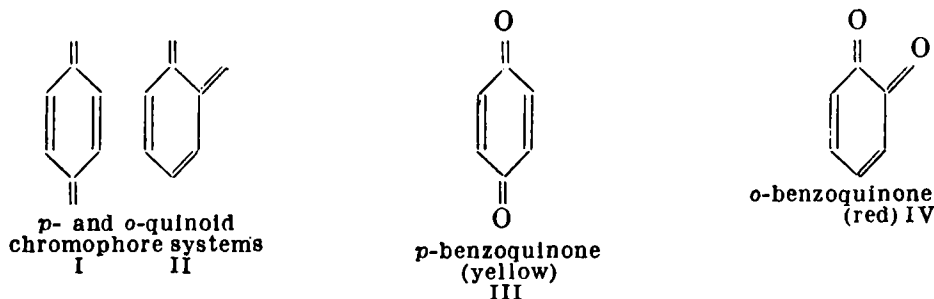
An even weaker, but nevertheless very important chromophore is the double bond $\text{>C}=\text{C}<$.

The colour theory of organic compounds was taken a step further by the notion of complex chromophores. The most important of these are the conjugated double-bond systems of acyclic or cyclic structure. As the conjugated chain grows longer, the absorption spectrum moves from the ultraviolet (short waves) towards the red end (longer waves). Three examples of coloured hydrocarbons are carotène, which is orange, lycopene, which is orange-red (p. 520), and diphenylhexadecaene $\text{C}_6\text{H}_5-(\text{CH}=\text{CH})_8-\text{C}_6\text{H}_5$, which is of a copper-red colour.

The benzene nucleus and aromatic hydrocarbons with condensed nuclei are complex chromophore systems of great importance in the chemistry of dyes. Benzene and naphthalene are themselves colourless, but on combining with other chromophores produce coloured substances.

Important types of complex chromophore systems are the *p*-quinoid (I) and *o*-quinoid (II) groups. They are contained, for example,

in *p*-benzoquinone (III) and in *o*-benzoquinone (IV):



To turn a coloured substance, or chromogen, into a dye, it is necessary to introduce into its molecule, in addition to the chromophores, additional groups called *auxochromes* (colour-intensifiers), which deepen the colour, i.e., shift the absorption band from the ultraviolet towards the red end of the spectrum. An affinity towards fibre arises at the same time. It is necessary, however, to distinguish between the effect of groups on colour and on affinity towards fibre (the ability to dye fibre), which depends upon many factors. Three typical auxochromes are the groups —NH_2 , —OH , and $\text{—N(CH}_3)_2$. The acidic groups $\text{—SO}_3\text{H}$ and —COOH are at present not regarded as auxochromes. They exert only an insignificant influence on colour, but play an important part in dyeing, imparting to the dye a solubility in water and an affinity towards woollen and silk fibres. Some dyes are taken up by cotton fabric directly. They are called *substantive dyes**.

Substances that make a colour fast are called *mordants*. Common mordants are aluminium acetate, ferric and cupric salts, compounds of tin, and tannin. In order to dye a fabric, it is immersed in a solution of the mordant and then treated with steam at high temperature. This hydrolyzes the substance used as mordant. The finely dispersed metal hydroxide produced by hydrolysis becomes attached to the fibre, and the dye combines with it to form an insoluble lacquer. Dyes that are thus made fast by mordants are called *mordant dyes*. By using different mordants, it is possible to impart different colours to a fabric by the same dye.

263. Natural and Synthetic Dyes. In the old days organic dyes were derived exclusively from plants and animals. Alizarin prepared from the roots of the madder plant has been used since time immemorial as a red dye; blue indigo was obtained from the indigo

* The first substantive dye was made and used in 1883 by O. Miller and S. Prokhorov at the Tryokhgornaya Textile Mills in Moscow. The dye was prepared by oxidizing potassium thiocyanate by potassium chlorate. It was named *canarine* because it gave fabrics a canary colour.

plant, and carmine, from dried insects inhabiting certain varieties of the cactus plant. The famous "purple of the ancients", used for royal robes and other expensive garments, was obtained from a sea-snail occurring along the shores of the Mediterranean; the sea-snail secretes colourless matter which, when exposed to light, is oxidized by the oxygen of the air and turns into a dye. The structure of this dye was established by Friedländer in 1909-11 (p. 550).

The first artificial dye (mauve) was obtained in Britain in 1856 by Sir William Perkin, who stumbled upon it when oxidizing aniline that was not pure. The industrial production of several other dyes, including alizarin and indigo, soon followed.

Many hundreds of dyes not occurring in nature were also synthesized. At present synthetic dyes have almost completely replaced natural dyes.

The early dye syntheses were quite accidental; it was only after the birth of Butlerov's structural theory, the establishment of the structure of benzene, and the determination of the structure and mode of formation of dye-stuffs that the development of the techniques for dye synthesis was placed on a sound scientific foundation.

Many thousands of individual dyes, belonging to various classes of compounds, have since been synthesized. Their classification and rational naming has been made difficult by the diversity of their chemical composition, methods of preparation, and areas of application. To make matters worse, Western firms have often marketed new dyes under arbitrary names, which have nothing in common with the composition or structure of the dye.

Two systems of dye classification are at present in use: a chemical and a technical system.

The chemical classification of dyes is based on common chromophore groups, structure, and chemical properties. Accordingly, dyes are divided into such groups as nitro dyes (with the nitro group as chromophore), nitroso dyes (with the nitroso group as chromophore), azo-dyes, arylmethane dyes, indigo and indigoid dyes.

The chemical classification is particularly convenient for studying the chemistry of dyes, developing rational methods of their preparation, and seeking new dyes.

The technical classification is based on the areas and methods of dye application. For example, the acid dye group unites all the dyes that dye wool from an acid bath, although chemically these may be compounds of the most varied composition: simple and complex azo-dyes, triphenylmethane dyes, derivatives of anthraquinone, etc. The technical classification gives an idea of the purpose of a dye and the principal methods of its application.

The following are the most important groups of dyes in the technical system: *direct* (substantive) dyes, which colour cellulose fi-

bres from neutral solutions; *sulphur* dyes, which colour cellulose fibres from aqueous solutions of sodium sulphide; *acid* dyes, which colour wool and silk from an acid bath; *mordant* dyes, which colour wool just as acid dyes do, but are made fast by subsequent treatment with, say, chromic salts; *vat* dyes, which colour cellulose fibres in the form of colourless reduction products (so-called leuce compounds) from a weakly alkaline solution (vat), with the subsequent formation of the dye directly on the fabric as a result of oxidation by the oxygen of the air, and *pigments* and *lacquers*, which are dyes that are insoluble in water and are often used in the form of salts (they are used extensively in the dye and varnish industry and in the printing industry).

A rational *dye nomenclature* has been evolved in the Soviet Union in accordance with this technical classification. The first word in the name of the dye indicates its group; the second, its colour. Letters following the name indicate the shade of the colour and/or special conditions of its application. Only in the case of some dyes have their historical names, which have become international, been preserved. This is true of indigo, thioindigo, fuchsin, congo red, and a few others.

Polycyclic Aromatic Compounds

Polycyclic, or polynuclear aromatic compounds are substances whose molecules contain two or more linked benzene rings.

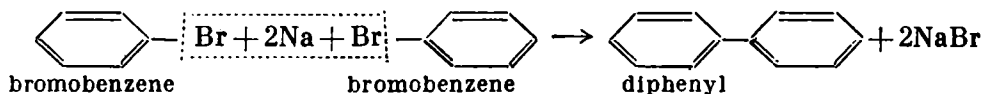
It is customary to distinguish two types of polycyclic aromatic compounds.

In one of them the benzene rings are linked either directly or by means of carbon atoms. In the other the rings are linked by common carbon atoms.

COMPOUNDS CONTAINING BENZENE RINGS LINKED THROUGH CARBON OR DIRECTLY

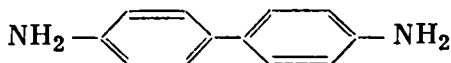
264. Diphenyl and Benzdine. The simplest compound with directly linked benzene rings is diphenyl $\text{C}_6\text{H}_5\text{—C}_6\text{H}_5$ (m.p. 70°). Its molecule consists of two interlinked benzene rings.

The structure of diphenyl is confirmed by the method of its preparation: by the action of metallic sodium upon bromobenzene.



Both benzene rings in diphenyl fully retain their properties.

The most important of the diphenyl derivatives is *benzdine*:

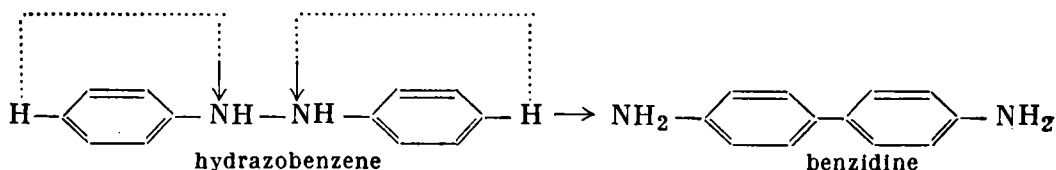


It was first prepared by Zinin in 1845.

As evident from its formula, benzdine is a diamine of diphenyl; the amino groups in it are in *p*-positions to the link between the benzene rings.

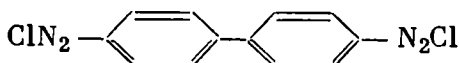
Benzdine may be prepared by treating hydrazobenzene with a strong mineral acid. This causes the hydrogen atoms in *p*-positions to the NH groups to join the nitrogen. Each of the NH groups therefore becomes an NH_2 group, the bond between the nitrogen

atoms is ruptured, and the benzene rings link up:

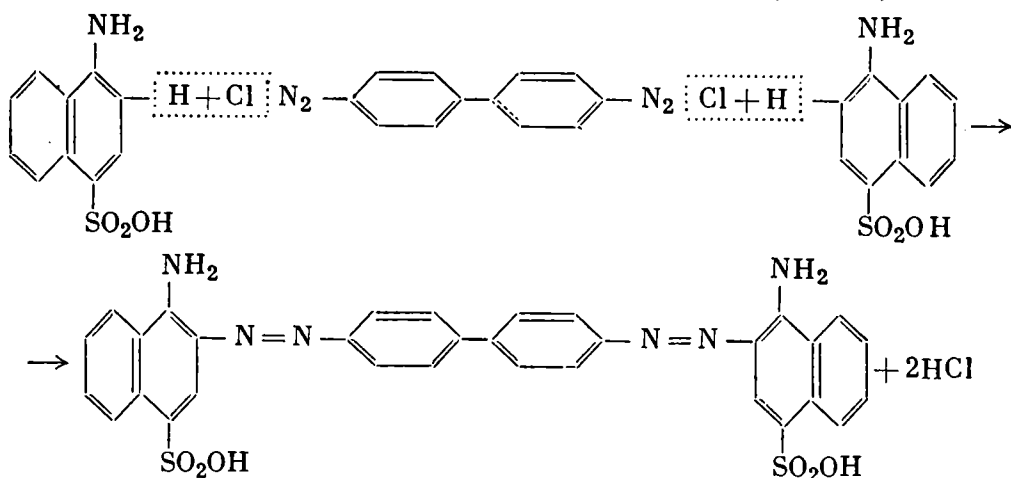


This is known as the *benzidine rearrangement*.

Like every primary aromatic amine, benzidine, upon treatment with nitrous acid, is diazotized and becomes a diazo-compound:



By coupling this diazo-compound with phenols and amines, substances are obtained that contain two azo-groups. These substances are important dyes; they can be used to dye cotton textiles directly (without mordant). One such dye is *congo red*. It is prepared by coupling diazotized benzidine with naphthionic acid (p. 488):



The dye is the sodium salt of this compound.

As is obvious from the name of the dye, it is red. The action of a mineral acid upon congo red produces its acid, which is blue.

To change the colour of congo red it is necessary to have a higher concentration of hydrogen ions than is needed to change the colour of methyl orange. Congo is therefore used as an indicator for strong (mineral) acids. The hydrogen ion concentration even in very dilute solutions of these acids will change the red colour of congo to violet, whereas organic acids (acetic) change its colour to blue only when their concentration is high.

265. Triphenylmethane and Its Derivatives. The simplest compounds containing benzene rings linked through carbon atoms are diphenylmethane, triphenylmethane, and tetraphenylmethane.

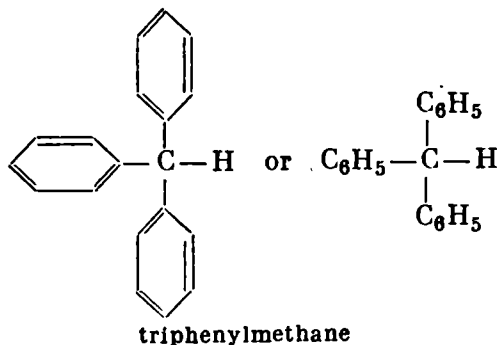
These hydrocarbons can be regarded as derivatives of methane, in whose molecule two or more hydrogen atoms have been replaced by phenyl groups.

The physical properties of the phenyl derivatives of methane, including toluene, are listed in Table 22.

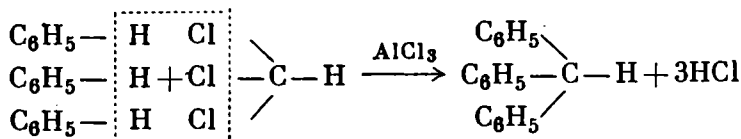
TABLE 22. Physical Properties of Phenyl Derivatives of Methane

Derivative	Formula	M.p., °C	B.p., °C
Toluene	$(\text{C}_6\text{H}_5)\text{CH}_3$	-95	110.6
Diphenylmethane	$(\text{C}_6\text{H}_5)_2\text{CH}_2$	26	262
Triphenylmethane	$(\text{C}_6\text{H}_5)_3\text{CH}$	92.5	359
Tetraphenylmethane	$(\text{C}_6\text{H}_5)_4\text{C}$	285	431

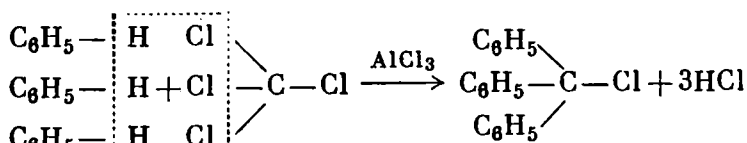
The most important of these compounds is *triphenylmethane* with its derivatives:



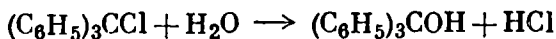
Triphenylmethane can be prepared by treating chloroform with benzene in the presence of anhydrous aluminium trichloride:



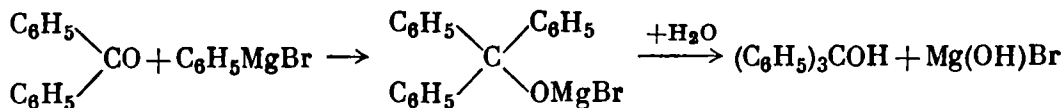
If carbon tetrachloride is taken instead of chloroform, the product is triphenylmethyl chloride:



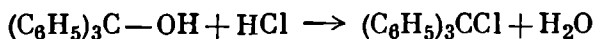
Triphenylmethyl chloride (colourless crystals) melts at 113° . It is easily decomposed by water to triphenylcarbinol:



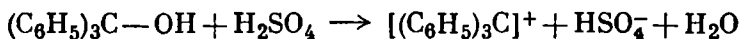
Triphenylcarbinol can also be prepared by treating benzophenone with phenyl-magnesium-bromide:



Triphenylcarbinol (colourless crystals) melts at 162.5° . The hydroxyl group in its molecule is very easily replaced by a halogen. When, for example, dry hydrogen chloride is passed through a solution of triphenylcarbinol in chloroform, triphenylmethyl chloride is formed:



Triphenylcarbinol and its derivatives have basic properties; they dissolve in concentrated mineral acids to form intensely coloured salts. When, for instance, triphenylcarbinol is dissolved in concentrated sulphuric acid, the solution acquires a yellow colour:



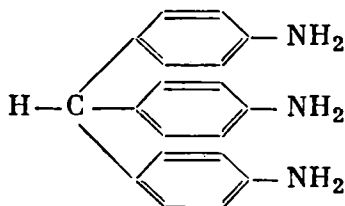
This coloured salt is, however, easily decomposed by water, and colourless triphenylcarbinol is precipitated.

In this, as in other cases, the appearance of a colour is due to changes in the structure of the molecule.

266. Triphenylmethane Dyes. Their Structure and Properties. Triphenylmethane is the parent substance of a series of dyes, which include the phthaleins (p. 439).

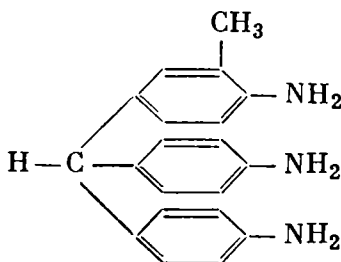
Especially important among the triphenylmethane dyes are the amino derivatives of triphenylmethane itself and of its homologues. Let us consider the distinctive features of substances of this group by examining several of its representatives: derivatives of triamino-triphenylmethane and triaminodiphenyltolylmethane.

Triaminotriphenylmethane can be regarded as a derivative of triphenylmethane, in each of whose benzene rings the hydrogen atom in *p*-position has been replaced by an amino group:



Triaminodiphenyltolylmethane is the closest homologue of the previous substance; it has a methyl group in *o*-position to an

amino group:

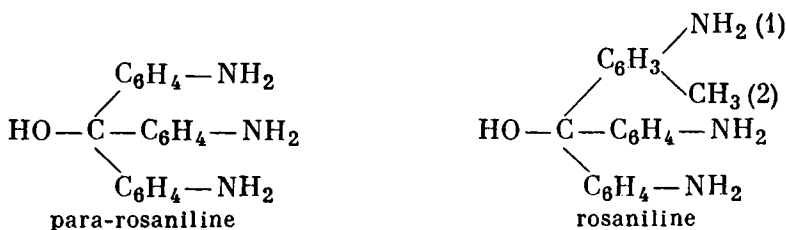


It should be pointed out that only amines with at least two amino groups, each in *p*-position to the methane carbon, can be converted to dyes.

The triphenylmethane amines are colourless substances. They are so-called *leuco bases of dyes*; oxidation easily converts them to hydroxy derivatives.

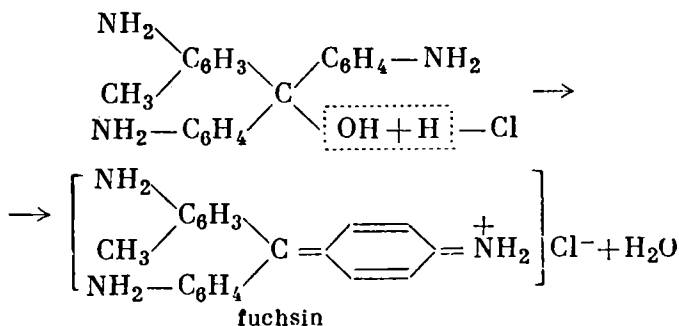
Triaminotriphenylcarbinol, called *para-rosaniline*, is obtained from triaminotriphenylmethane by this procedure.

The oxidation of triaminodiphenyltolylmethane yields *rosaniline*:



These hydroxy derivatives are called *pseudo bases of dyes*.

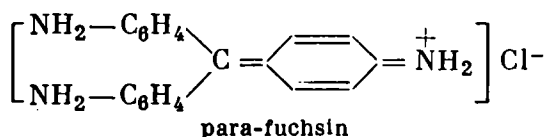
Their treatment with acids causes the following process to take place:



In other words, water is released and one of the benzene rings acquires a quinoid structure*. This results in salt-like substances with the properties of dyes.

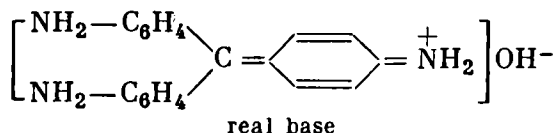
* The question of how the structural formulas of these dyes should be written cannot be considered settled finally.

Rosaniline in this case yields *fuchsin*, while para-rosaniline yields *para-fuchsin*:



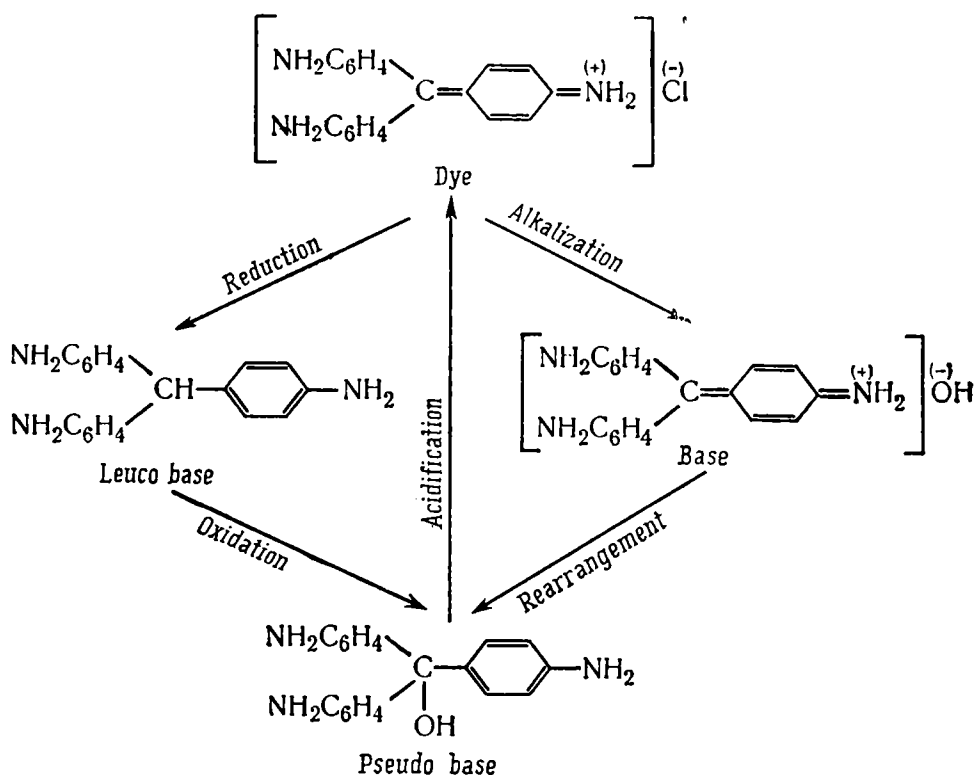
These dyes cannot be regarded as salts of the substances from which they are obtained by the action of acids. That is why the hydroxy derivatives are not real bases of the dyes, but pseudo bases.

The treatment of the dyes with alkalis at first produces coloured real bases, such as



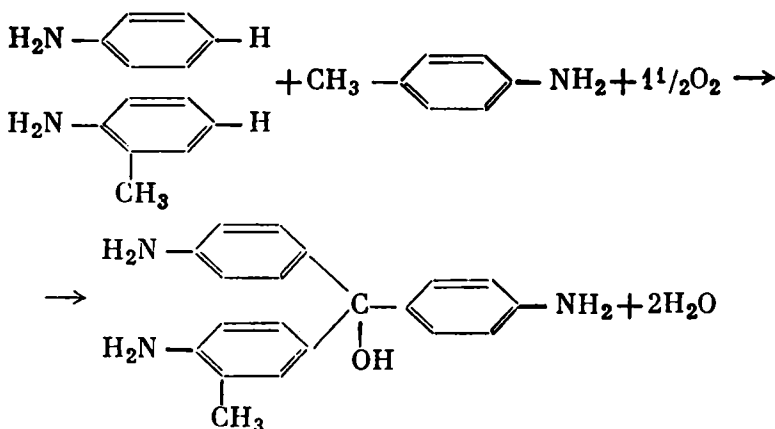
These are very soon converted to colourless pseudo bases.

Reduction turns the triphenylmethane dyes into colourless leuco bases. The transformations of the triphenylmethane dyes when treated with acids or alkalis, and also through reduction, can be represented by the following diagram:



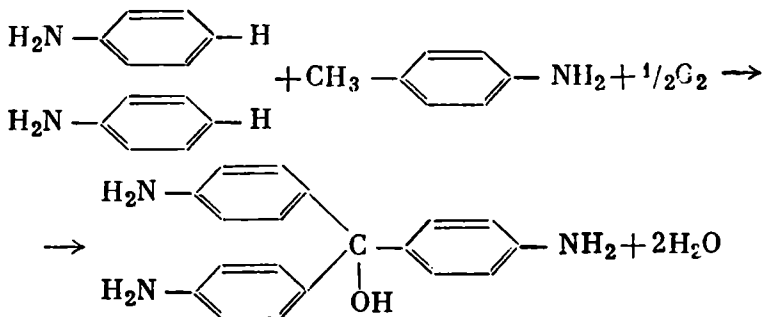
267. Preparation of Triphenylmethane Dyes. The triphenylmethane dyes can be prepared by two methods: by the oxidation of monocyclic aromatic derivatives and by a condensation reaction involving diphenylmethane derivatives. The first method yields fuchsin, para-fuchsin, and Malachite green; the second, crystal violet.

Fuchsin can be prepared by oxidizing a mixture of aniline, *o*-toluidine, and *p*-toluidine, the methane carbon atom being formed by the CH_3 group of the *p*-toluidine molecule:



This results in rosaniline, which, upon treatment with hydrochloric acid, yields fuchsin.

Para-fuchsin is prepared by oxidizing a mixture of *p*-toluidine and aniline:



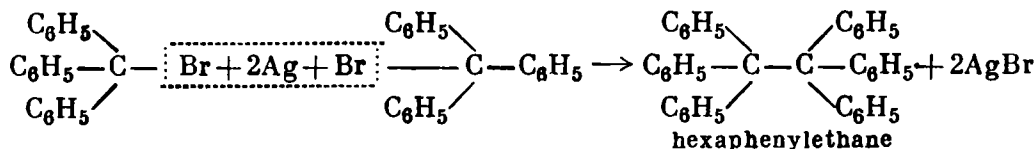
Para-rosaniline reacts with hydrochloric acid to form para-fuchsin.

Fuchsin forms crystals which have a greenish lustre; with water it gives a deep red solution. When an excess of concentrated hydrochloric acid is added to the solution, it acquires a yellow-orange colour, which is reconverted to red by dilution with water.

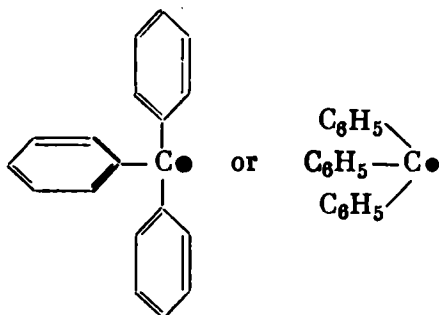
The introduction of methyl groups into the molecules of fuchsin and para-fuchsin produces violet dyes; the introduction of phenyl groups produces blue dyes.

268. Free Radicals. In 1900 Gomberg, by treating triphenylmethyl bromide with silver powder or zinc dust in the complete absence of

air, obtained hexaphenylethane:

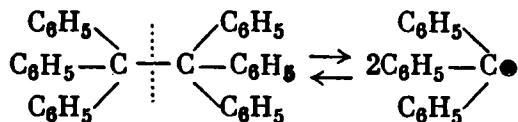


The colourless crystals of hexaphenylethane upon dissolving, say, in benzene give a yellow solution. The solution is oxidized extremely readily and reacts instantly with bromine or iodine, yielding $(\text{C}_6\text{H}_5)_3\text{CBr}$ or $(\text{C}_6\text{H}_5)_3\text{CI}$. Neither of these reactions is typical of ordinary hydrocarbons. Further investigation revealed the presence in the solution of the free radical triphenylmethyl:



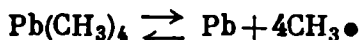
In this radical the central carbon atom (designated by a black circle) is trivalent.

The following equilibrium exists in the solution:



This means that hexaphenylethane dissociates into two free radicals, which has been confirmed by determining the molecular weight of hexaphenylethane in molten naphthalene at 80° . The molecular weight of hexaphenylethane is 486, while that of triphenylmethyl is 243. The experimental value of the molecular weight corresponded to a 30% dissociation of the hexaphenylethane in the solution. A rise in temperature increased the percentage of triphenylmethyl in the solution.

Other substances too were obtained that break up into radicals with a trivalent carbon atom. Some of them even at ordinary temperature are completely dissociated into radicals. In these substances the trivalent carbon atom is linked to groups with a high molecular weight. Finally, in 1929 Paneth and Hofeditz proved (by the thermal decomposition of tetramethyllead) that a free methyl radical could survive for a short time (thousandths of a second):



To detect light free radicals Paneth and Hofeditz devised a mirror technique. A swift stream of pure hydrogen (or nitrogen) under a pressure of 1-2 mm was saturated with tetramethyllead vapour by passage through test-tube 1 (Fig. 68) containing $\text{Pb}(\text{CH}_3)_4$ cooled by means of solid carbon dioxide.

The gas is then passed through the long quartz tube 2 and pumped off through trap 3 immersed in liquid air. At first, by heating the tube locally at section 4, a lead deposit, or mirror, is obtained there; the tube is then heated at another point 5, closer to the gas inlet, while section 4 is left cold. A fresh mirror is

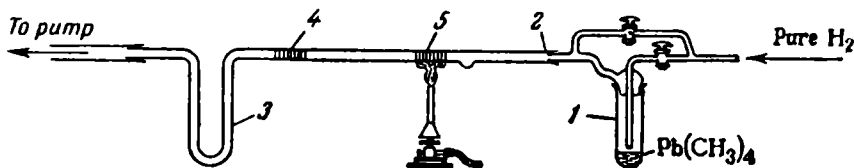


Fig. 68. Apparatus for preparing free alkyl radicals:

1—test-tube; 2—quartz tube; 3—trap; 4—lead mirror; 5—heated section of tube.

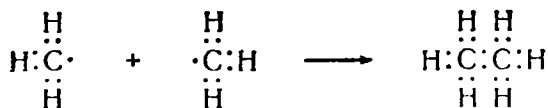
then formed at 5, while the first mirror disappears at the same time (provided the distance between 4 and 5 does not exceed 30 cm). From this it follows that one of the products of the thermal decomposition of $\text{Pb}(\text{CH}_3)_4$ in section 5 is a gas capable of reacting with the cold metallic lead in section 4. This gas can only be free methyl CH_3 , since it has been established experimentally that none of the other gaseous decomposition products—hydrogen, methane, or ethylene—has any effect on a lead mirror.

In 1931 Paneth and Lautsch by the same procedure obtained the free ethyl radical C_2H_5 from tetraethyllead.

By drawing upon electron notions, we can represent the structure of the free methyl radical as follows:



Free radicals therefore have an unpaired electron, carry no electric charge (are not ions), and are capable of combining with one another (recombination of radicals):



Numerous investigations by Soviet and foreign scientists (N. Semyonov and co-workers, A. Terenin, V. Kondratyev, F. Rice, R. Norrish, Waters and many others) have made it plain that very many chemical reactions, such as oxidation, polymerization, the thermal decomposition of hydrocarbons, syntheses based on water gas, etc., take place with the intermediate formation of unstable free radicals.

The idea of the existence of free radicals forms the corner-stone of the so-called chain theory of chemical processes. In several cases the existence of short-lived free radicals has been directly corroborated by spectroscopic data.

CONDENSED-NUCLEI COMPOUNDS

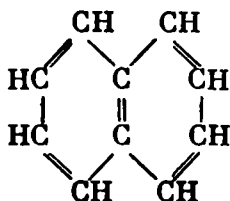
269. Naphthalene. The simplest aromatic compound with joined (condensed) nuclei is naphthalene $C_{10}H_8$.

Naphthalene crystallizes in glistening leaflets; it melts at 80° and boils at 218° . It is practically insoluble in water and has a characteristic odour. Despite its high boiling point, it is very volatile and sublimes readily.

Naphthalene is prepared from that part of coal-tar which is distilled in the 170 - 230° temperature range and which is called carbolic oil. The oil is treated with a sodium hydroxide solution (to remove phenols) and then distilled; the distillate, consisting chiefly of naphthalene, solidifies almost completely. It is pressed and washed with an acid and with a sodium hydroxide solution; final purification of the naphthalene is effected by steam distillation or sublimation.

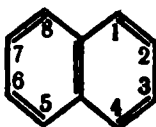
A comparison of the compositions of naphthalene ($C_{10}H_8$) and the saturated hydrocarbon with ten carbon atoms in the molecule ($C_{10}H_{22}$) reveals that the naphthalene molecule is fourteen hydrogen atoms short of complete saturation. In spite of this, naphthalene enters readily into substitution reactions, which is a characteristic feature of aromatic compounds.

The elementary composition of naphthalene was established by A. Voskresensky. Erlenmeyer subsequently proposed the following structural formula for it:

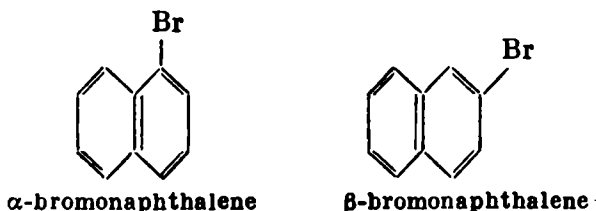


According to this formula, the naphthalene molecule consists of two benzene rings linked in such a way that they have two neighbouring carbon atoms in common.

The structure of naphthalene is very often expressed by a simplified formula, in which the carbon atoms that have hydrogen atoms attached are numbered as follows:

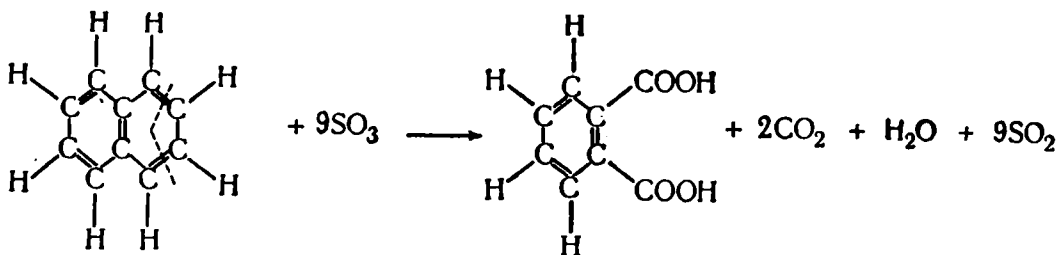


The replacement of a hydrogen atom in the naphthalene molecule by another atom, say, a halogen atom, can give rise to two series of derivatives. Substitution can either take place at a carbon atom linked directly to one of the two common carbon atoms (substitution at carbon atoms 1, 4, 5, or 8). These naphthalene derivatives are designated by the letter α . Or else substitution can take place at carbon atoms 2, 3, 6, or 7. Such naphthalene derivatives are designated by the letter β :



Two isomers are thus possible for the monosubstituted naphthalene derivatives.

Strong oxidizing agents convert naphthalene to phthalic acid $C_6H_4(COOH)_2$. For many years this oxidation was accomplished industrially by heating naphthalene with fuming sulphuric acid in the presence of mercuric sulphate as a catalyst:



This is accompanied by the reduction of sulphur trioxide to sulphur dioxide, while phthalic acid is subsequently converted to phthalic anhydride.

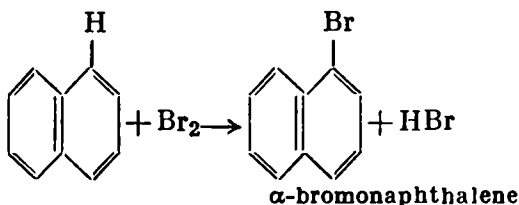
The need for mercuric sulphate in this reaction was discovered accidentally. A thermometer happened to break in an experiment that involved the sulphonation of naphthalene, and the mercury poured into the sulphonation mixture. To the surprise of the chemist conducting the experiment, phthalic anhydride in the form of smoke began to issue from the apparatus.

A more refined technique for oxidizing naphthalene to phthalic anhydride was evolved in 1918. Naphthalene vapour mixed with air in this case passed at 450° through tubes with a V_2O_5 catalyst.

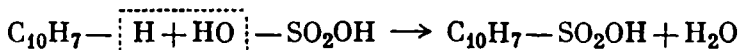
Naphthalene is hydrogenated by hydrogen in the presence of catalysts more readily than benzene is (see p. 389).

270. Naphthalene Derivatives. Numerous derivatives of naphthalene are known.

As far as the action of halogens is concerned, naphthalene can be brominated and chlorinated, with α -derivatives being formed first of all:

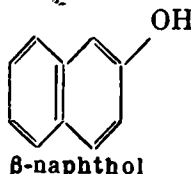
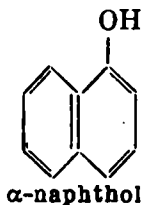
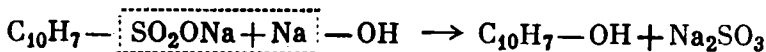


Treatment with strong sulphuric acid causes the sulphonation of naphthalene, i.e., the substitution of the sulfoxyl $\text{—SO}_2\text{OH}$ for hydrogen. The reaction produces *naphthalenesulphonic acids* $\text{C}_{10}\text{H}_7\text{—SO}_2\text{OH}$:



Either α - or β -naphthalenesulphonic acid is formed, depending on the conditions in which the reaction is conducted. If it takes place at a low temperature (60°), the principal product is α -naphthalenesulphonic acid; at a high temperature (160°) the chief product is β -naphthalenesulphonic acid, since the α -acid is at that temperature converted to the β -acid.

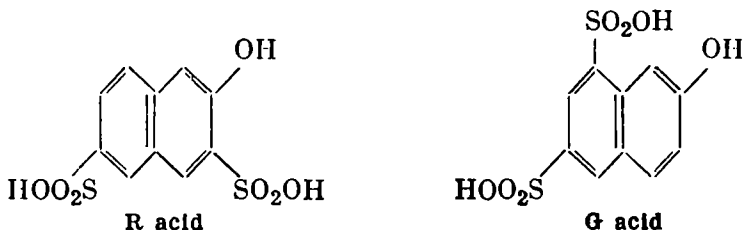
The fusing of sulphonic acid salts with caustic alkalis causes the replacement of the sulfoxyl by the hydroxyl; this produces hydroxy derivatives known as the *naphthols* $\text{C}_{10}\text{H}_7\text{—OH}$:



In properties the naphthols resemble the phenols. Like the phenols, they dissolve in caustic alkalis and give a characteristic colour with ferric chloride. An aqueous solution of α -naphthol gives a violet precipitate with ferric chloride; β -naphthol gives a green colour.

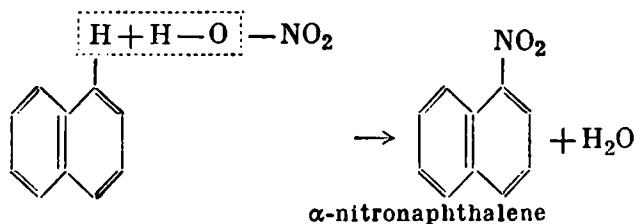
The *naphtholsulphonic acids* play an important part in dye manufacture. Two examples of these acids are 2-naphthol-3,6-disulphonic acid and 2-naphthol-6,8-disulphonic acid. The former is called R

acid; the latter, G acid:



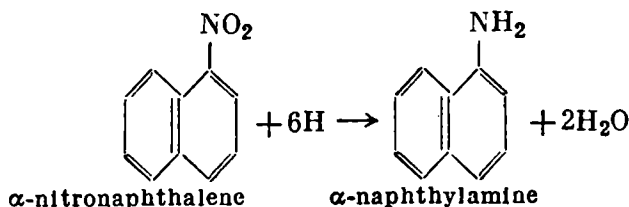
As a component of dye molecules, R acid imparts a red colour to them, while G acid imparts yellow tinges*.

When naphthalene is treated with concentrated nitric acid, the hydrogen group H is substituted for hydrogen. The reaction product is α -nitronaphthalene $\text{C}_{10}\text{H}_7\text{—NO}_2$:



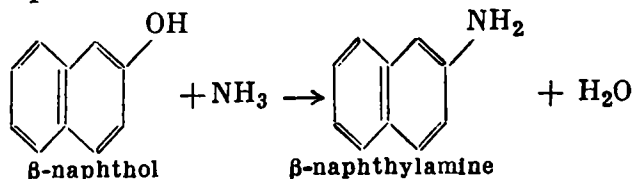
Beta-nitronaphthalene is more difficult to obtain and is prepared by a different method.

The naphthalene amino derivatives $\text{C}_{10}\text{H}_7\text{—NH}_2$ are called *naphthylamines*. Alpha-naphthylamine is prepared by reducing α -nitronaphthalene:



It was first obtained by Zinin (p. 447).

To prepare β -naphthylamine, β -naphthol is heated under pressure with ammonia and calcium chloride or zinc chloride, as well as with ammonium sulphate:



Commercial α -naphthylamine has the disagreeable odour of faeces; β -naphthylamine is odourless.

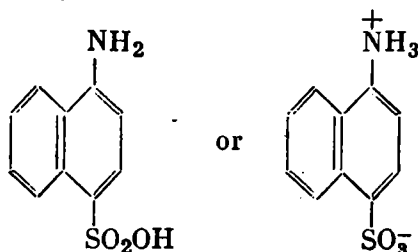
* R and G stand for the German words *rot* and *gelb*.

The physical properties of some of the naphthalene derivatives are listed in Table 23.

TABLE 23. Physical Properties of Naphthalene Derivatives

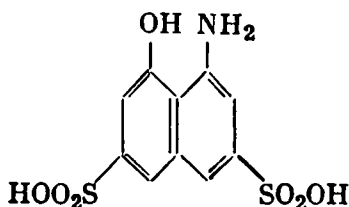
Derivative	Formula	M. p., °C	B. p., °C
α -Chloronaphthalene	$C_{10}H_7Cl$	-17	259
β -Chloronaphthalene	$C_{10}H_7Cl$	56.7	266
α -Bromonaphthalene	$C_{10}H_7Br$	6.2	281
β -Bromonaphthalene	$C_{10}H_7Br$	59	281
α -Nitronaphthalene	$C_{10}H_7NO_2$	61.5	304
β -Nitronaphthalene	$C_{10}H_7NO_2$	79	165
			(at 15 mm Hg)
α -Naphthalenesulphonic acid	$C_{10}H_7SO_2OH$	88	—
β -Naphthalenesulphonic acid	$C_{10}H_7SO_2OH$	83	—
α -Naphthol	$C_{10}H_7OH$	96	288
β -Naphthol	$C_{10}H_7OH$	122	294
α -Naphthylamine	$C_{10}H_7NH_2$	50	301
β -Naphthylamine	$C_{10}H_7NH_2$	113	306.1

In their chemical character the naphthylamines resemble aniline: they have weak basic properties and undergo nitration, sulphonation, etc. For example, by sulphonating α -naphthylamine it is possible to obtain *naphthionic acid*:



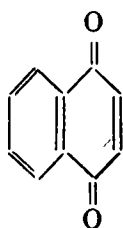
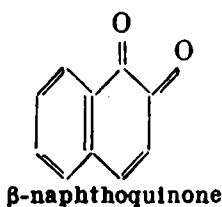
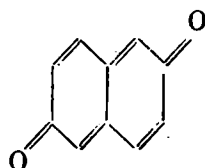
Naphthionic acid is practically insoluble in water, but dissolves in it readily in the presence of soda; this is due to the formation of its highly soluble sodium salt.

Another naphthalene derivative containing the amino group is 1-amino-8-naphthol-3,6-disulphonic acid, or H acid:



This is one of the most important intermediates in dye manufacture.

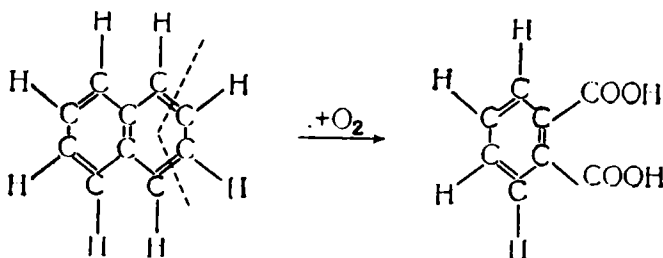
The quinones of naphthalene are called *naphthoquinones*. Three of these are known:

 α -naphthoquinone β -naphthoquinone

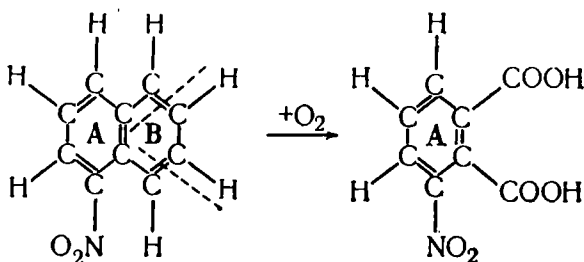
anthra-naphthoquinone

The naphthoquinones can be prepared by oxidizing the corresponding aminonaphthols. The naphthoquinones are crystalline coloured substances; α -naphthoquinone is yellow, while the two others are red. Alpha-naphthoquinone is highly volatile and has a pungent odour.

271. Proof of the Structure of Naphthalene. The structure of naphthalene is confirmed by the oxidation of its derivatives. The oxidation of naphthalene yields phthalic acid:



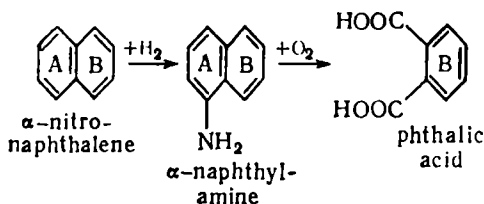
Similarly, the oxidation of α -nitronaphthalene yields nitrophthalic acid:



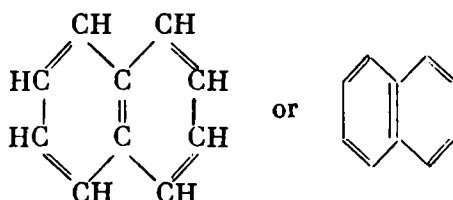
Consequently, the naphthalene molecule contains the benzene ring A.

The reduction of α -nitronaphthalene yields naphthylamine. It is quite obvious in this case that the naphthylamine is α -naphthylamine and that the NH_2 group is in the same ring that contained the NO_2 group.

If α -naphthylamine is oxidized, the product is phthalic acid:

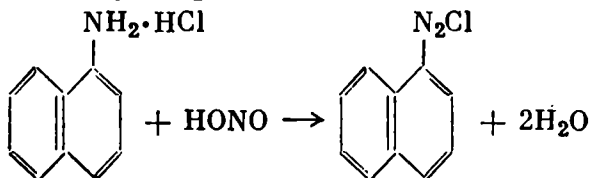


This involves the break-up of the ring A. Consequently, the naphthalene molecule, in addition to the benzene ring A, contains the benzene ring B, i.e., the structure of naphthalene corresponds to the formula:



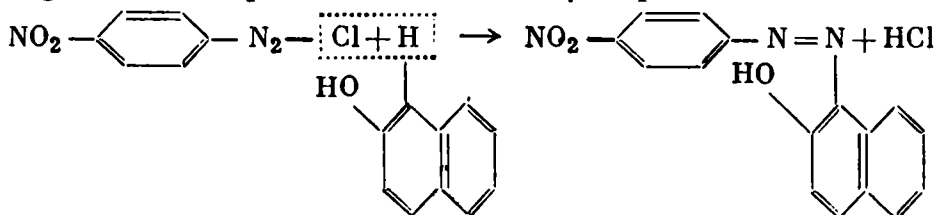
It should also be mentioned that the presence of first-class substituents (NH_2 , etc.) increases, while the presence of second-class substituents (NO_2 , etc.) decreases, the reactivity of this benzene ring.

272. Naphthalene Dyes. Like other aromatic amines, the naphthylamines are diazotized by nitrous acid to diazo-compounds. The diazotization of α -naphthylamine, for instance, yields α -naphthyl diazonium chloride $\text{C}_{10}\text{H}_7\text{N}_2\text{Cl}$:



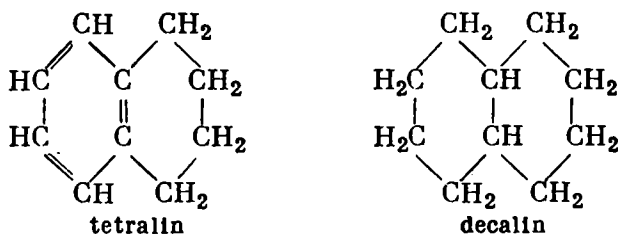
The diazo-compounds of the naphthalene series are chemically similar to the diazo-compounds of the benzene series. Like them, the diazo-compounds of the naphthalene series react with naphthols and amines to form amino- and hydroxyazo-compounds, many of which are very important dyes. Some dyes are prepared by coupling diazo-compounds of the benzene series with naphthols and naphthylamines.

One of the naphthalene dyes is *para-red*, which is prepared by coupling diazotized *p*-nitroaniline with β -naphthol:



The dye is applied to fabrics in the following way. The fabric is soaked in an alkaline solution of β -naphthol, dried, and then immersed in an ice-cold solution of diazotized *p*-nitroaniline; the insoluble dye is formed on the fabric itself. This is known as *glacial*, or *ice, dyeing*, since the process is conducted under ice-cold conditions to avoid decomposition of the diazo-compounds.

273. Tetralin and Decalin. When naphthalene is heated with hydrogen in the presence of a nickel catalyst under pressure, hydrogen is added to naphthalene. Two addition products are formed, *tetralin* $C_{10}H_{12}$ and *decalin* $C_{10}H_{18}$:

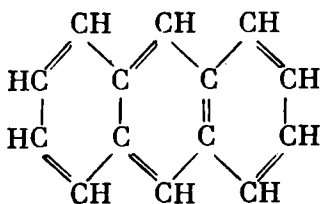


Tetralin and decalin are liquids that are lighter than water. The former boils at 207.6° ; the latter, at about 190° . They are used as solvents for lacquers.

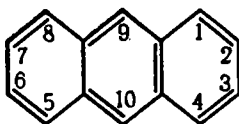
274. Anthracene. Anthracene $C_{14}H_{10}$ is obtained from the coal-tar fraction boiling above 270° and known as anthracene oil.

It crystallizes in white leaflets with a blue fluorescence, melts at 217° , boils at 354° , and is insoluble in water.

Anthracene has the following structural formula:



Its structure is commonly expressed by a simpler formula, in which the carbon atoms that have hydrogen attached to them are numbered as follows:



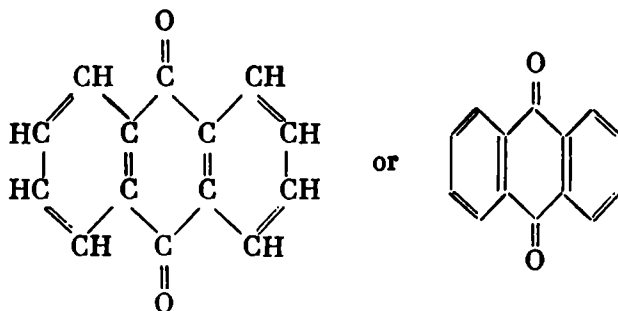
As is evident from this formula, the carbon atoms with hydrogen attached may be divided into three groups according to their position: the positions 1, 4, 5, and 8 are designated by the letter α ; the positions 2, 3, 6, and 7, by the letter β , and the positions 9 and 10,

by the letter γ . Three isomers are therefore possible for monosubstituted anthracene derivatives.

275. Anthraquinone. When anthracene is treated with chromic acid mixture, it is oxidized to anthraquinone $C_{14}H_8O_2$.

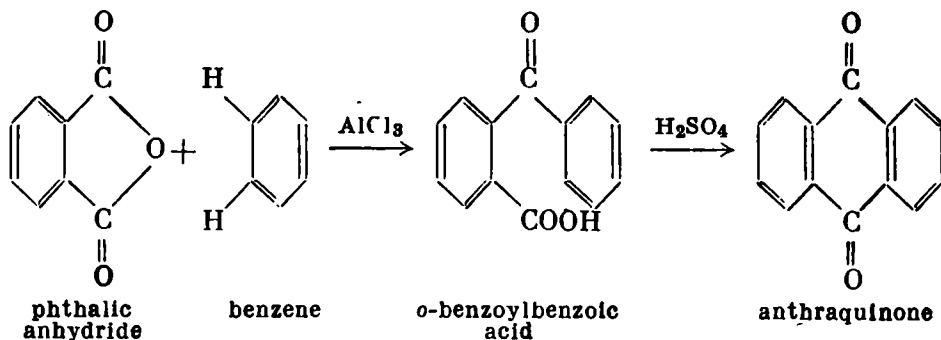
Anthraquinone forms yellow crystals; it melts at 286° , boils at 382° , sublimes readily, is insoluble in water, and undergoes oxidation with difficulty.

Its structure is expressed by the formula:



This structure of anthraquinone is confirmed by its synthesis from phthalic anhydride and benzene. The reaction is conducted in two stages.

First the phthalic anhydride reacts with benzene in the presence of aluminium trichloride to form *o*-benzoylbenzoic acid; this, upon treatment with concentrated sulphuric acid, yields anthraquinone:

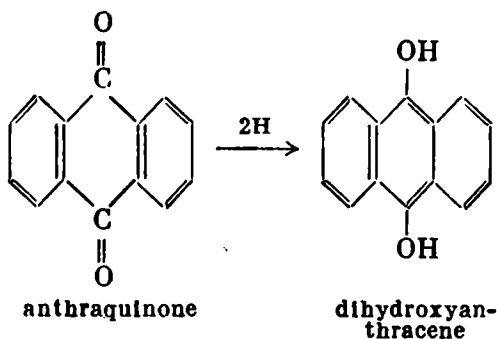


This reaction, like the oxidation of anthracene, serves for the industrial production of anthraquinone. Anthraquinone may be prepared by oxidizing anthracene by the oxygen of the air at $400\text{--}500^\circ$ in the presence of catalysts (V_2O_5 , etc.).

Anthraquinone can be brominated, nitrated, and sulphonated.

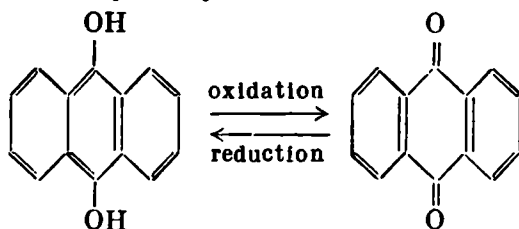
M. Ilyinsky discovered that when anthraquinone is sulphonated in the presence of as much as a small amount of mercury, the sulphonyl is directed almost exclusively into α -position. If, on the other hand, sulphonation is conducted in the absence of mercury, the product is a β -sulphonic acid. This makes it possible to obtain the α -acid practically without admixtures of the β -isomer.

By means of zinc dust or gaseous hydrogen in the presence of nickel in an alkaline medium anthraquinone is rapidly reduced to dihydroxyanthracene:



Dihydroxyanthracene dissolves in alkalis, producing a blood-red solution. When the solution is exposed to air, the colour disappears and anthraquinone is precipitated.

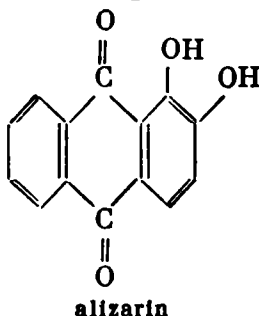
The reaction of dihydroxyanthracene oxidation is reversible:



The oxidation of dihydroxyanthracene by air is accompanied by the formation of hydrogen peroxide. This reaction serves as the basis for the industrial production of hydrogen peroxide.

276. Alizarin. The principal derivative of anthraquinone is alizarin $C_{14}H_8O_4$. It forms red needles, melts at 290° , and sublimes readily. Alizarin is practically insoluble in water. It is one of the most important dye-stuffs and has been used for dyeing since time immemorial.

The structure of alizarin is expressed by the formula:

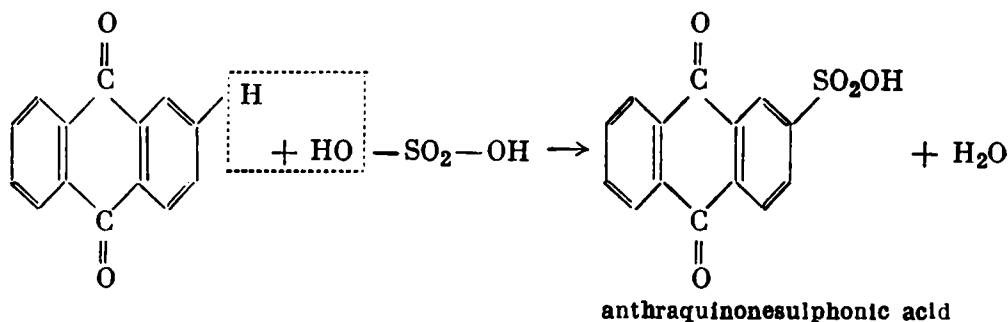


It is a typical mordant dye. With aluminium as mordant, it dyes cotton a bright red; with ferric hydroxide it gives a dark violet colour, and with chromic hydroxide, a green varnish.

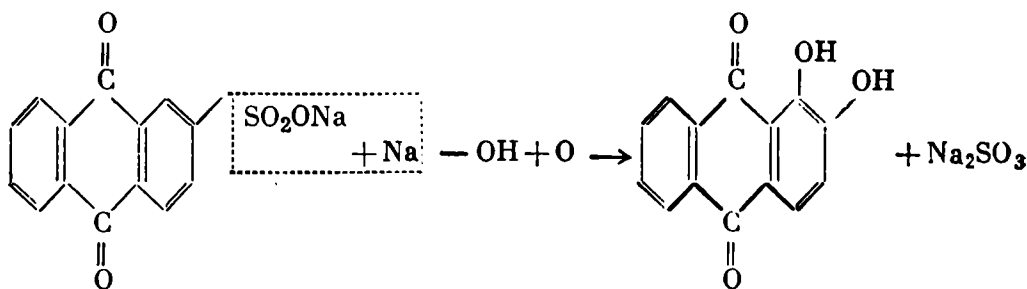
Up to 1869 alizarin was derived from the roots of the madder plant, which was grown in the south of France and in the Caucasus. In 1868 C. Graebe and C. Liebermann found that by heating with zinc dust, alizarin can be reduced to anthracene. This provided the necessary information for establishing the structure of alizarin. Earlier it had been found that alizarin forms esters whose molecules contain two monocarboxylic acid residues and that it dissolves in alkalis, i.e., that alizarin is a dihydroxy phenol. The composition of anthracene is expressed by the formula $C_{14}H_{10}$; the composition of anthraquinone, by the formula $C_{14}H_8O_2$, and the composition of alizarin, by the formula $C_{14}H_8O_4$. From these facts Graebe and Liebermann deduced that alizarin was a dihydroxy derivative of anthraquinone, and they proved their deduction correct by synthesizing alizarin. This was the first synthesis of a dye occurring in the vegetable kingdom.

The factory production of synthetic alizarin began in 1869, i.e., immediately after Graebe and Liebermann's work. The industrial method of its manufacture devised in 1873 is, with some modifications, employed to this day. Basically, the method consists in the following.

The sulphonation of anthraquinone yields anthraquinonesulphonic acid:



Alizarin is then obtained by fusing the sodium salt of this acid with sodium hydroxide in the presence of potassium chlorate or saltpetre, which act as oxidizing agents:



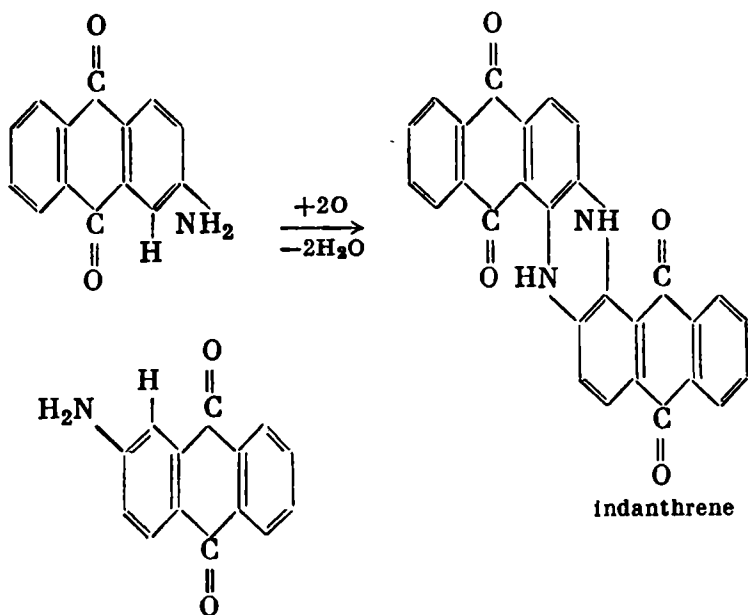
The synthetic alizarin produced by this method has completely replaced the natural product. Whereas in the seventies of the past century the annual harvest of madder ran to 500,000 tons a year, today the plant can only be seen in collections and museums.

In his book *The Origin and Development of Organic Chemistry*, Schorlemmer wrote: "The discovery of artificial alizarin not only affected farming, but had an even greater influence on the production of coal-tar, caustic soda, and potassium chlorate; as for sulphur trioxide, used to obtain sulphonic acid, its production gave rise to an entirely new branch of the chemical industry."

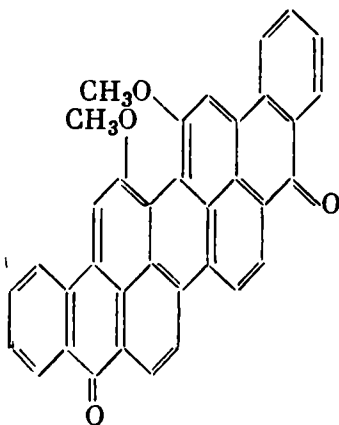
The establishment of the structure of alizarin and its synthesis were the first application of structural theory to practical problems. This theory was the beacon that guided Graebe, Liebermann, and other scientists in their research, and we see how brilliantly it was borne out by practice.

The synthesis of alizarin produced a very great impression. It gave a powerful impetus to the study of dye-stuffs, which resulted in several discoveries of major importance to both science and industry. Thanks to this research, we now know very many anthraquinone derivatives, besides alizarin, which are excellent dyes; these dyes do not occur in the plant world.

277. Polycyclic Vat Dyes (Indanthrenes). When β -aminoanthraquinone is fused with potassium hydroxide and saltpetre as an oxidizing agent at 220° , the product is a dye known as *indanthrene*, or *vat blue O*:



A more complex dye derived from anthraquinone is *indanthrene violet*:



indanthrene violet

Many other indanthrenes are known; their structure is similar to that of indanthrene and indanthrene violet. Anthraquinone and its derivatives in most cases serve as the material for their preparation.

These dyes have a high molecular weight and contain a big percentage of carbon and a low percentage of hydrogen; they are insoluble in water, are not volatile, and have high melting points. As regards fastness, they have practically no rivals.

Anthraquinone can be converted by reduction to dihydroxyanthracene, which is soluble in alkalis and which is oxidized by the oxygen of the air to insoluble anthraquinone again. Similarly, the reduction of indanthrene causes hydrogen to be added to the carbonyl oxygen. This results in hydroxy derivatives of indanthrenes, which are soluble in alkalis. The alkaline solutions, upon exposure to air, again produce indanthrenes.

Indanthrene dyeing is conducted in the following manner. The indanthrenes are reduced by sodium hyposulphite in an alkaline solution. The cloth is immersed in this vat, kept there for some time, and then exposed to air. The oxygen of the air oxidizes the alkaline solution on the cloth, and the dye has its dyeing effect on the cloth, the colour acquired by the cloth sometimes being markedly different from the colour of the vat.

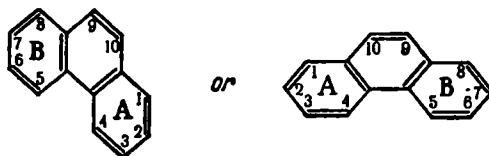
This method of dyeing, in which the dye is formed on the cloth itself through the oxidation of an alkaline solution by the oxygen of the air, is called *vat dyeing*.

The most ancient of the vat dyes is indigo (p. 548).

278. Phenanthrene. Phenanthrene $C_{14}H_{10}$ is an isomer of anthracene and, like the latter, occurs in coal-tar.

It forms colourless crystals, melts at 101° , and boils at 340° .

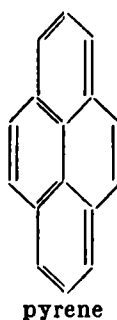
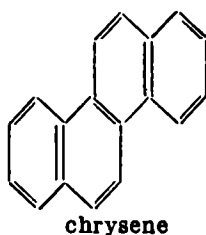
The structure of phenanthrene is expressed by a formula which can be written in two different ways:



The two formulas are identical. Each of them shows, in the first place, that the phenanthrene molecule contains two directly linked benzene rings (A and B) and, secondly, that each of the rings is connected in *o*-position with a $-\text{CH}=\text{CH}-$ group, which, together with some of the carbon atoms of the first two rings, forms a third six-membered ring.

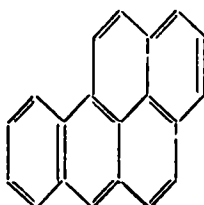
Phenanthrene has no industrial applications, but is of great interest because certain natural substances of tremendous physiological importance are closely related to it, e.g., various steroids, vitamin D, and sex hormones.

279. Hydrocarbons with Many Condensed Benzene Rings. Coal-tar contains the hydrocarbons *chrysene* $\text{C}_{18}\text{H}_{12}$ (m.p. 255°) and *pyrene* $\text{C}_{16}\text{H}_{10}$ (m.p. 156°):



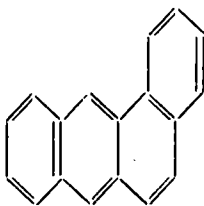
It is easy to see that both hydrocarbons have the phenanthrene ring system.

Coal-tar also contains an insignificant amount of 1,2-benzpyrene $\text{C}_{20}\text{H}_{12}$:



1,2-Benzpyrene possesses carcinogenic properties, i.e., produces cancer.*

Several other carcinogenic hydrocarbons, besides 1,2-benzpyrene, are known; most of them contain the ring system of 1,2-benzanthracene:



1,2-benzanthracene

When deposited on the skin, they produce cancer of the skin; the subcutaneous injection of these hydrocarbons causes cancer of the connective tissue.

* In recent years chemists have made a thorough investigation of the tar-like substance obtained from tobacco smoke. It was found to contain, in addition to nicotine, aromatic hydrocarbons of the benzpyrene type with pronounced carcinogenic properties. When deposited on the skin or introduced into the lungs of mice, it produced malignant tumours.

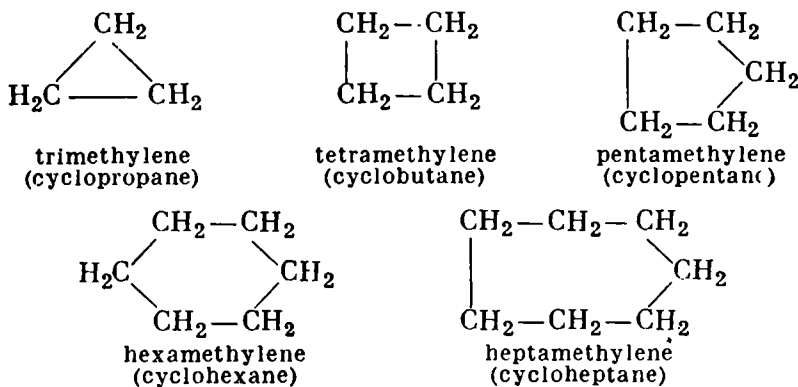
ALICYCLIC COMPOUNDS

Alicyclic hydrocarbons are hydrocarbons with a ring structure, but not of the benzene type. Most of them differ in chemical character only very slightly from corresponding compounds of the aliphatic division. This accounts for the name alicyclic, i.e., aliphatic cyclic hydrocarbons.

CHAPTER XX

Cycloparaffins

280. Structure of Cycloparaffins and Their Preparation. The cycloparaffins are also referred to as cycloalkanes or polymethylene hydrocarbons. Their composition corresponds to the formula C_nH_{2n} , i.e., they have the same composition as corresponding hydrocarbons of the ethylene series. The molecules of the principal cycloparaffin hydrocarbons consist of CH_2 methylene groups whose carbon atoms are interlinked:

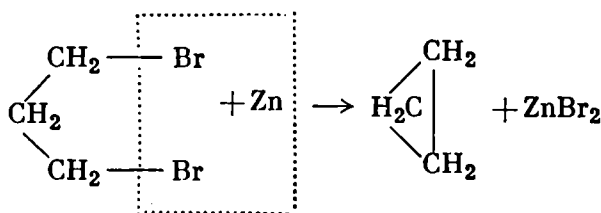


Cyclopentane and cyclohexane derivatives are contained in petroleum. For this reason the cycloparaffins are often called naphthenes.

Many of the cycloparaffins were isolated from Baku petroleum and synthesized by Markovnikov and Zelinsky*.

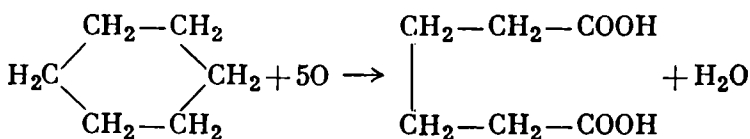
A prominent part in the study of the cycloparaffins was also played by many other Russian chemists: G. Gustavson, N. Demyanov, M. Konovalov, N. Kizhner, S. Namyotkin, B. Kazansky, and others.

The cyclic structure of these hydrocarbons is confirmed both by the methods of their preparation and by their properties. Cyclopropane, for example, can be prepared by the action of zinc on 1,3-dibromopropane:

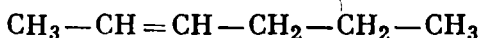


This reaction was discovered by Gustavson.

The cyclic structure of hexamethylene is confirmed by the fact that its oxidation produces the dicarboxylic adipic acid:



If hexamethylene were not cyclic and were an ethylene hydrocarbon



its oxidation would not yield a dicarboxylic acid with the same number of carbon atoms; there would, instead, be a rupture of

* Nikolai Zelinsky (1861-1953) was born in the town of Tiraspol on February 6, 1861. In 1884 he completed a course of studies at the Natural Science Department of the Novorossiisk University in Odessa. In 1888 he became a lecturer there. His M.Sc. dissertation (in 1889) was entitled "On Isomerism in the Thiophene Series", while his D.Sc. dissertation (in 1891) bore the title "Studies of Stereoisomerism Phenomena in Saturated Carbon Compounds".

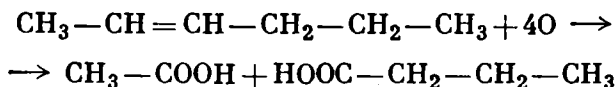
In 1893 Zelinsky took over the chair of organic and analytical chemistry at Moscow University, where he worked until his death (July 31, 1953).

In 1926 Zelinsky was elected a corresponding member of the U.S.S.R. Academy of Sciences, and in 1929, a full member.

Zelinsky founded a most extensive school: his pupils include such outstanding chemists as L. Chugayev, N. Shilov, S. Namyotkin, A. Nesmeyanov, B. Kazansky, A. Balandin, and V. Sadikov, not to mention many others. Zelinsky's scientific work was highly diverse: with his pupils he published some 500 papers.

Most of them deal with the chemistry of the hydrocarbon and of petroleum, specifically with the synthesis and properties of various saturated and unsaturated cyclic hydrocarbons. Well known, too, is Zelinsky's invention of the first charcoal gas mask, which saved the lives of many thousands of people. He likewise did very important work in synthesizing liquid fuel on the basis of carbon monoxide.

the chain and the products would be acids with fewer carbon atoms:

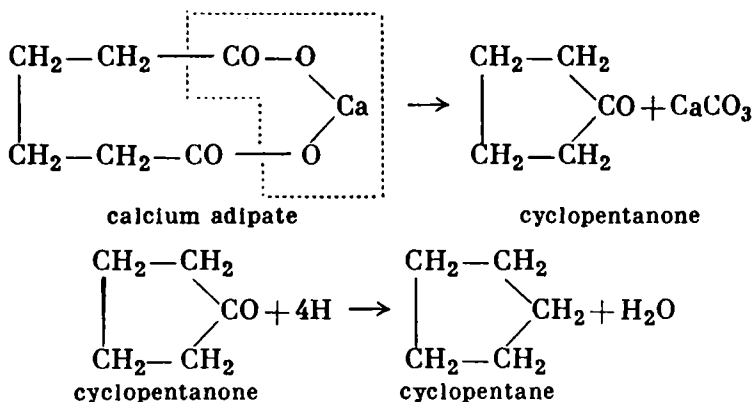


The fact that the oxidation of cyclohexane produces a dicarboxylic acid with the same number of carbon atoms in the molecule is clinching proof of the cyclic structure of the substance.

The synthesis of cycloparaffins can be effected by several methods:

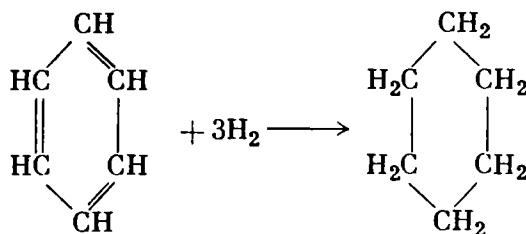
1. By detaching the halogen from dihalogen derivatives in which the halogen atoms are attached to other than neighbouring carbon atoms, e.g., by the Gustavson reaction.

2. By the dry distillation of the calcium salts of dicarboxylic acids. This at first produces a ketone, which is then reduced to a hydrocarbon:



By means of thorium salts, L. Ruzicka in the same way obtained ketones containing up to thirty carbon atoms in a ring.

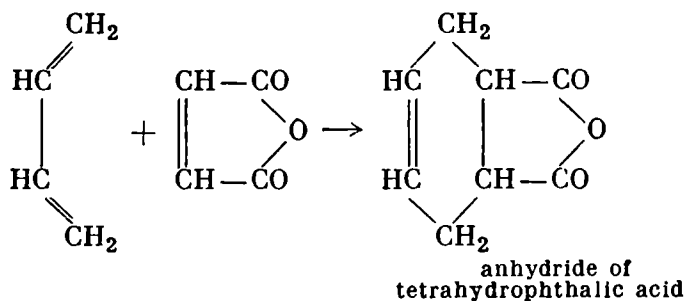
3. Cyclohexane and its derivatives can be prepared by hydrogenating corresponding compounds of the aromatic division:



For this purpose a mixture of hydrogen and the vapour of the substance to be hydrogenated is led over metallic catalysts: nickel, platinum, palladium.

Many unsaturated alicyclic compounds with six-membered rings have lately been prepared by the condensation of conjugated dienes with various unsaturated compounds (acids, their anhydrides, aldehydes, or ketones) in whose molecules the double bond is situated

directly between two carbonyls or two carboxyls. This is illustrated by the condensation of butadiene with maleic anhydride:



In these reactions the extreme carbon atoms of the conjugated system link up with carbon atoms of the other unsaturated compound, a double bond arising between the middle carbon atoms of the conjugated system. The synthesis of substances on the basis of this reaction is called a *diene synthesis*.

281. Properties of Cycloparaffins. Cyclopropane and cyclobutane are gases; the intermediate cycloparaffins are liquids, and the higher ones are solids.

The physical properties of some of the cycloparaffins are listed in Table 24.

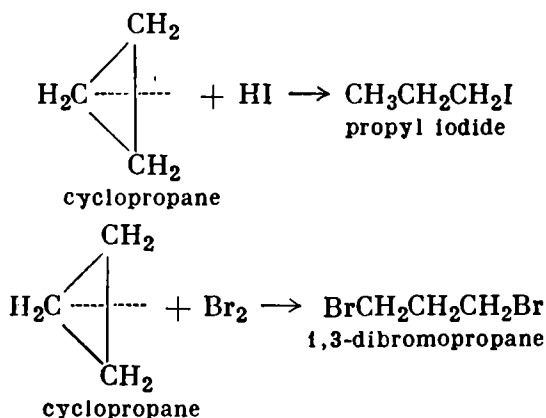
Although the cycloparaffins have two hydrogen atoms fewer than saturated hydrocarbons, they are very similar to them in properties. They are highly resistant to the action of oxidizing agents. The addition of bromine in most cases takes place very slowly, if at all.

TABLE 24. Physical Properties of Cycloparaffins

Cycloparaffin	Formula	M.p., °C	B.p., °C	Relative density at 20°
Cyclopropane . . .	C ₃ H ₆	-127.6	-32.8	0.720 (at -79°)
Cyclobutane . . .	C ₄ H ₈	-90	12.6	0.7038
Cyclopentane . . .	C ₅ H ₁₀	-93.2	49.5	0.7454
Cyclohexane . . .	C ₆ H ₁₂	6.5	80.7	0.7786
Cycloheptane . . .	C ₇ H ₁₄	-8.1	118.5	0.811
Cyclooctane . . .	C ₈ H ₁₆	14.8	150.6 (at 709 mm Hg)	0.8362

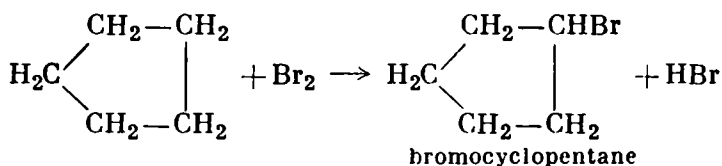
This is due to the stability of the cycloparaffin rings. Rings consisting of five or six carbon atoms are especially stable. The cyclopropane ring, however, is easily ruptured by the action of hydrogen iodide or

bromine:



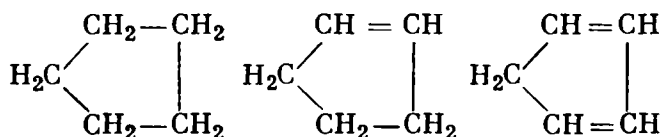
Cyclopentane and cyclohexane rings are ruptured with great difficulty. For example, it is only at 305-310° that cyclopentane adds hydrogen in the presence of platinum, becoming normal pentane, whereas the cyclopropane ring is ruptured in the presence of the same catalyst without any heating. For an explanation of the different stability of cyclic compounds see pp. 226 and 508.

282. Some Representative Cycloparaffins. *Cyclopentane* C_5H_{10} is a component of certain types of petroleum. It is a colourless mobile liquid, which boils at 49.5°. Cyclopentane reacts with bromine in the light to form bromocyclopentane:



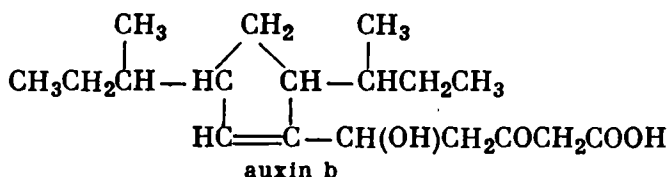
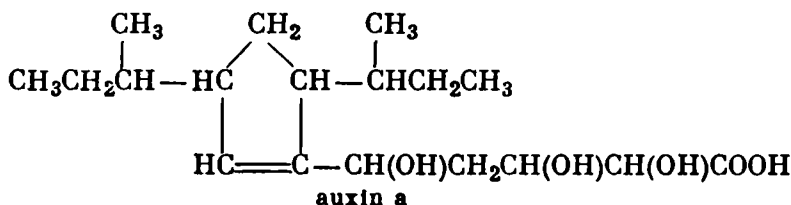
Some of the *naphthenic acids*, which are contained in large amounts in Caucasian petroleum, are carboxyl derivatives of cyclopentane. Their composition is expressed by the general formula $\text{C}_n\text{H}_{2n-1}\text{COOH}$. The naphthenic acids are compounds whose hydrocarbon radical contains a cycloparaffin ring. One such acid is methylcyclopentanecarboxylic acid, first isolated from petroleum by Markovnikov. Sodium salts of naphthenic acids are formed when paraffin oil and certain other petroleum cuts are purified with alkali. These salts can produce a foam and have a detergent effect. The commercial product is known as *naphtha soap*.

The unsaturated hydrocarbons corresponding to cyclopentane C_5H_{10} are cyclopentene C_5H_8 and cyclopentadiene C_5H_6 :



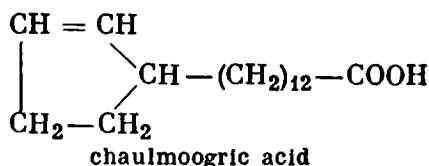
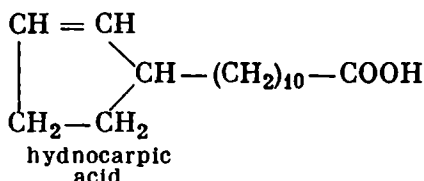
Cyclopentene can be prepared by treating bromocyclopentane with alcoholic potassium hydroxide. It is a liquid, which boils at 44° and has all the properties of an olefine.

The most important of the cyclopentene derivatives are the *auxins*, plant growth stimulators:



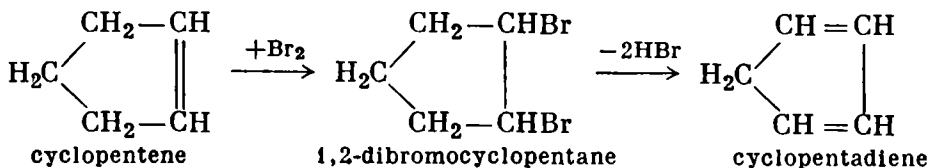
They are contained in all plants. It is interesting that certain other substances, entirely different in composition and structure (see p. 417), have an effect similar to that of the auxins.

Hydnocarpic acid and *chaulmoogric acid*



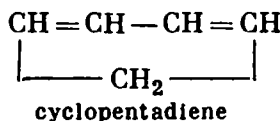
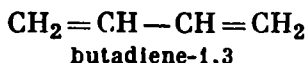
are contained as glycerides in chaulmoogra oil, which occurs in the seeds of certain plants that grow in East Asia, Africa, and South America. Both substances have a pronounced bactericidal action. Their salts and ethyl esters are used in the treatment of leprosy.

Cyclopentadiene is formed in the destructive distillation of coal and is contained in crude petrol. It was synthesized by Zelinsky and co-workers. By adding bromine to cyclopentene, they prepared 1,2-dibromocyclopentane. When this was then heated to 182° with fused sodium acetate and acetic acid, cyclopentadiene was formed:

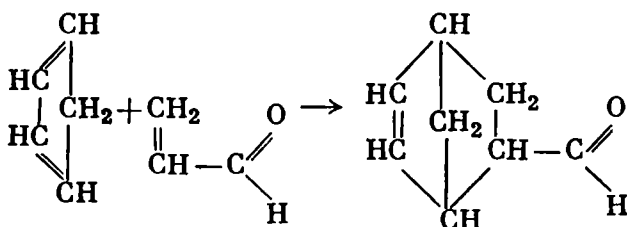


Cyclopentadiene is a colourless liquid, which boils at 42.5° . Its molecule contains a system of conjugated double bonds. The

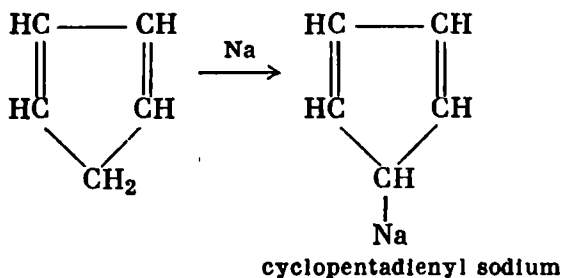
compound can be regarded as a methylene derivative of butadiene-1,3:



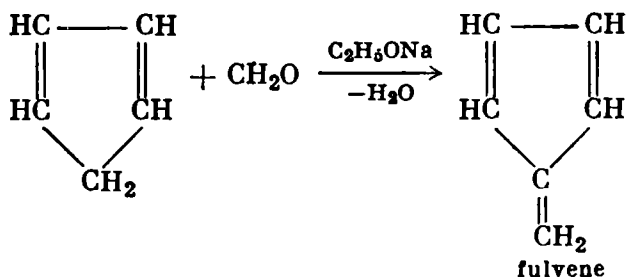
Like other diene compounds, cyclopentadiene polymerizes readily. Its molecules are added to the molecules of many unsaturated compounds. With acrolein, for instance, it forms a derivative of tetrahydrobenzaldehyde:



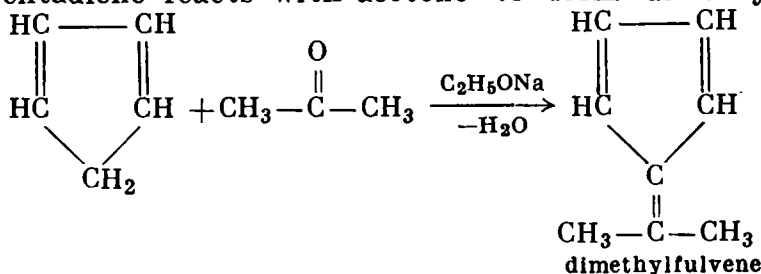
The hydrogen atoms of the methylene group are easily substituted. In boiling xylene, for example, cyclopentadiene reacts with powdered sodium to form cyclopentadienyl sodium:



Cyclopentadiene condenses with aldehydes and ketones to form coloured hydrocarbons called *fulvenes*. With formaldehyde the product is fulvene:

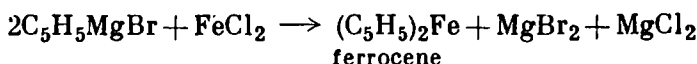


Cyclopentadiene reacts with acetone to form dimethylfulvene:

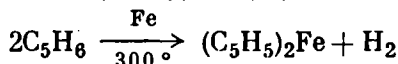


Fulvene itself is very unstable, but its homologues are quite stable and have been studied thoroughly. The colours of the fulvenes range from pale yellow in the case of fulvene to deep red in the case of diphenylfulvene. The fulvenes very readily add oxygen.

In 1951 Panus prepared a derivative of cyclopentadiene called dicyclopentadienyl iron, or, more often, *ferrocene*. It can be prepared from an organomagnesium compound of cyclopentadiene and ferrous chloride:



Another, simpler method of preparing ferrocene is by leading gaseous cyclopentadiene over reduced iron at 300°:

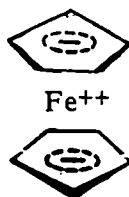


Ferrocene (yellowish orange crystals) melts at 174°. It is extremely stable and can be heated to 470° or boiled with aqueous solutions of HCl or NaOH without decomposition. It is easily sublimed, does not dissolve in water, and dissolves in organic solvents. Fundamental studies of the chemical changes of ferrocene have been carried out by Nesmeyanov.

In substitution reactions ferrocene behaves just as benzene or phenol. It enters into the Friedel-Crafts reaction, can be sulphonated, enters into the Mannich reaction (condensation with formaldehyde), and into the azo coupling reaction (an aldehyde group can be introduced into it). The hydrogen atoms of one or both rings can be substituted. Ferrocene thus exhibits the properties whose sum-total is regarded by chemists as the *characteristic of an aromatic compound*.

Ferrocene was one of the first *non-benzoid aromatic compounds* to be prepared. It was followed by similar compounds of cyclopentadienyl with other metals: Co, Mo, Ni, Mn, Cr, Ti, V, Ru, etc. Later it was established that aromatic hydrocarbons (benzene and others) also form stable crystalline substances with metals and that these substances are similar to ferrocene.

By means of X-ray analysis it was established that ferrocene has a two-plane structure symmetric with respect to a centre. The iron atom is situated in the centre between the two parallel cyclopentadienyl rings at an equal distance from all ten carbon atoms.



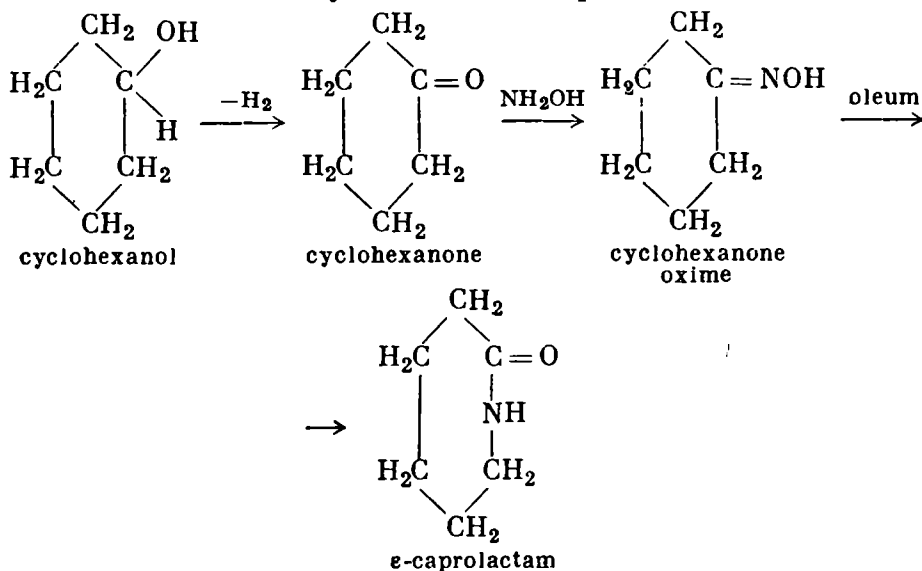
The distances between the carbon atoms in each ring are the same and equal 1.41 Å, i.e., are very close to the distances between the carbon atoms in benzene (1.39 Å). The iron atom is a dipositive ion, while the rings are negatively charged. As a result, the molecule as a whole is electrically neutral. All 12 π -electrons link the rings and the iron atom.

Compounds related to ferrocene, such as dicyclopentadienyl cobalt and dicyclopentadienyl nickel, and also dibenzene chromium and its analogues, are of a similar structure. This new type of complex compounds has been given the name "sandwich compounds".

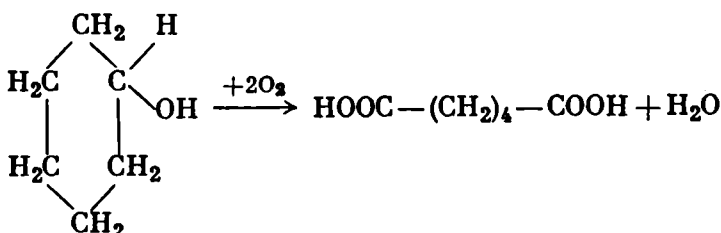
Cyclohexane C_6H_{12} occurs in considerable amounts in Caucasian and West-Ukrainian petroleum. It can be synthesized by hydrogenating benzene. Cyclohexane is a colourless liquid with a petrol odour; it boils at 80.7°.

Cyclohexanol $C_6H_{11}(OH)$ is manufactured industrially by hydrogenating phenol. It is a liquid with an odour somewhat like that of camphor and boils at 161°.

Cyclohexanol is an important intermediate in the production of synthetic polyamide fibres. By catalytic dehydrogenation it can be converted to a cyclic ketone, *cyclohexanone*. Cyclohexanone reacts with hydroxylamine to yield cyclohexanone oxime, whose rearrangement under the influence of oleum produces ϵ -caprolactam, the initial monomer for the synthetic fibre *capron*:



The oxidation of cyclohexanol by nitric acid or, catalytically, by the oxygen of the air produces adipic acid:



Adipic acid is used to produce polyester resins and certain plasticizers. Large quantities of it are used to manufacture polyamide fibres of the *nylon* type.

Cyclohexanol is used on a limited scale as a solvent.

283. Strain in Alicyclic Compounds. To account for the great stability of the pentamethylene and hexamethylene rings, as well as the low stability of cycles consisting of four and, especially, of three carbon atoms (and of ethylene and acetylene hydrocarbons), A. Baeyer* advanced the so-called strain theory (p. 226).

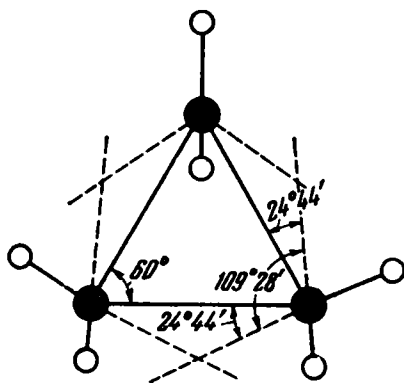


Fig. 69. Deviation of valencies in a three-membered cycle.

Figs. 23 and 24 (p. 252) show chains of three, four, and five carbon atoms. It is clear from these figures that for a cycle of three carbon atoms to close, the direction of the valencies of the carbon atoms has to be altered. As for a five-membered cycle, it closes without any deviation of the valencies.

Let us calculate the angle of deviation for these bonds in various cycles. Since the bonds between the carbon atoms in a three-membered cycle form an equilateral triangle, the angle between them equals 60° (Fig. 69); and since the angle between the direction of the valencies in a tetrahedron is $109^\circ 28'$, the angle of the deviation for each

* Adolf von Baeyer (1835-1917) was an outstanding German chemist who worked at Berlin and Strasbourg.

His many papers in diverse fields of organic chemistry dealt with such subjects as the establishment of the structure of pyrrole and indole, the establishment of the structure and the first synthesis of indigo (1880), and investigations of acetylene, aromatic, and alicyclic hydrocarbons, which led him to postulate the strain theory (1885).

In 1870 Baeyer suggested that the assimilation of carbon by the green parts of plants proceeded through the intermediate formation of formaldehyde, which subsequently polymerizes into saccharoid substances.

valency equals

$$\frac{109^{\circ}28' - 60^{\circ}}{2} = 24^{\circ}44'$$

In a four-membered cycle the valencies form a square.

Consequently, the angle of deviation is

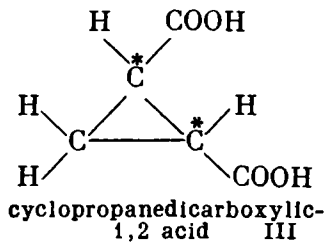
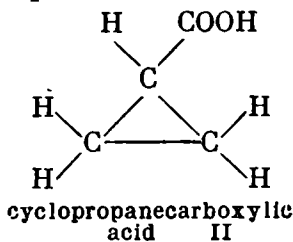
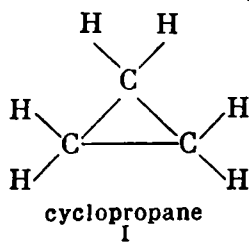
$$\frac{109^{\circ}28' - 90^{\circ}}{2} = 9^{\circ}44'$$

Each of the inner angles of a pentagon equals* 108° . Hence, the angle of deviation is $0^{\circ}44'$ (Fig. 70). The same calculations for six- and eight-membered cycles, on the assumption that all the carbon atoms lie in the same plane, yield the values of $5^{\circ}36'$ and $12^{\circ}51'$ respectively (Fig. 71).

The tetrahedral arrangement of bonds, with the angles between them equal to $109^{\circ}28'$, is the most stable. The angle of deviation from this direction is, according to Baeyer's theory, a measure of "strain", i.e., a measure of the instability of the cycle.

It follows from Baeyer's theory that a six-membered cycle ought to be less stable than a five-membered cycle, while the higher cycles ought to be as unstable as the trimethylene ring. This is not in accordance with the facts: a six-membered cycle is no less stable than a five-membered cycle. Moreover, many cycles with a very large number of carbon atoms are known to be quite stable. This contradiction was removed when it was established that—beginning with the six-membered ring—the carbon atoms forming the cycle do not lie in the same plane. This means that cycles of many carbon atoms can be formed without any deviation of the valencies, i.e., without any strain (Fig. 72). Such cycles experience no Baeyer strain.

284. Stereoisomerism of Alicyclic Compounds. A carbon atom in a ring is asymmetric if it is linked to two different atoms of radicals and to two different remainders of the ring. This can be illustrated by the case of cyclopropane:



* Each inner angle of a regular polygon equals $\frac{2d(n-2)}{n}$, where n is the number of sides that the polygon has.

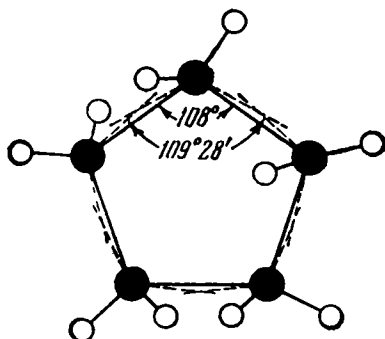


Fig. 70. Deviation of valencies in a five-membered cycle.

If one hydrogen atom in the cyclopropane molecule (I) is replaced by a carboxyl, the carbon atom at which the substitution took place does not become asymmetric, because two of its valencies are saturated by two absolutely identical remainders of the ring (II). But if carboxyl substitution takes place at two carbon atoms, both of them become asymmetric, since each is now connected with unequal remainders of the ring (III); at the same time it is easy to see that the two asymmetric carbon atoms are equivalent. As in the case of the

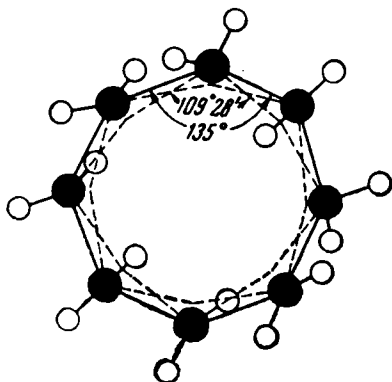


Fig. 71. Deviation of valencies in an eight-membered cycle.

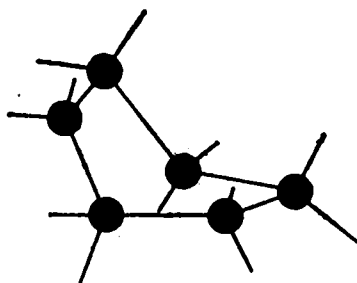
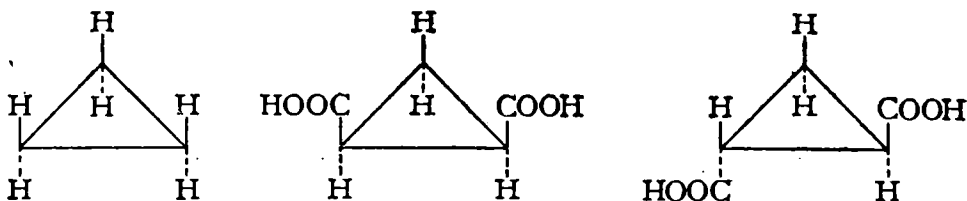


Fig. 72. Pattern of six-membered ring without strain.

tartaric acids, four isomers are possible: two optical antipodes, a modification that is inactive owing to internal compensation, and a racemic compound.

The configurations of the stereoisomers can be deduced in the following way. Since the carbon atoms in the cyclopropane molecule lie in the same plane, three of the six hydrogen atoms should be on one side of the plane of the ring, and the other three, on the other side. If two carbon atoms of the cyclopropane molecule each have one hydrogen atom replaced by a carboxyl, the hydrogen atoms may happen to be either on the same side of the plane (*cis*-configuration) or on different sides (*trans*-configuration):

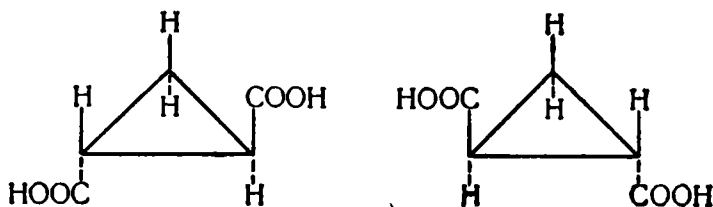


The *cis*-modification of cyclopropanedicarboxylic-1,2 acid melts at 139°; it gives up water to form an anhydride. The melting point of the racemic *trans*-modification is 175°; its anhydride is unknown.

The molecule of *cis*-cyclopropanedicarboxylic-1,2 acid is symmetric, and the acid is therefore optically inactive. The molecule of

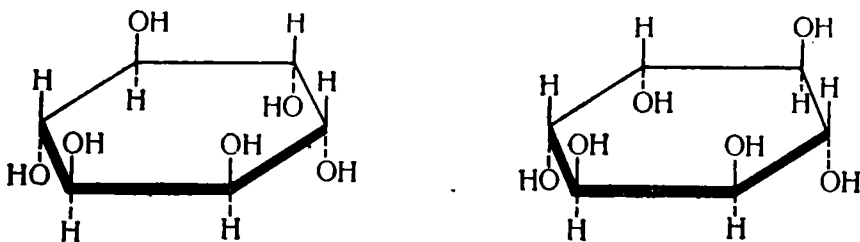
trans-cyclopropanedicarboxylic-1,2 acid has no plane of symmetry and does not coincide with its mirror reflection; two optical antipodes, as well as a racemic modification, are therefore possible in this case.

The optical antipodes of the *trans*-acid ($[\alpha]_D^{27} = \pm 84.8^\circ$)



were obtained by dividing the racemic modification by means of an optically active base (brucine).

Highly interesting, too, is the isomerism of *inositol* (hexahydroxycyclohexane) $C_6H_6(OH)_6$. Although its molecule has no asymmetric carbon atom, optically active forms of inositol are known. The molecules of optically active substances are not symmetric: they have no plane of symmetry and cannot be superimposed on their mirror images. Given at least one asymmetric carbon atom, a molecule is asymmetric. Yet in the case of inositol the molecule is asymmetric without a single asymmetric carbon atom. Eight stereoisomers are possible for inositol. Seven of them have symmetric molecules and are optically inactive, but the eighth stereoisomer, in whose molecule the 1,2,4-hydroxyls are on one side of the ring, while the 3,5,6-hydroxyls are on the other, is known in the form of two optical antipodes:



The molecules of these antipodes have no plane of symmetry; as mirror images of each other, they cannot be superimposed. The methyl esters of both laevorotatory inositol and dextrorotatory inositol occur in certain resins. One of the inactive, symmetrically arranged inositols, called *mesoinositol*, is found both in animal organisms (e.g., in the muscular fluid of the heart, in the liver, and in the brain substance—in the form of complex compounds) and in plants. In plants it occurs in the form of inositolphosphoric acid, i.e., an acid ester of phosphoric acid. It is isolated from plants, e.g., from hempen cake, in the form of a calcium salt known as *phytine*. Mesoinositol is a sweet crystalline substance.

Terpenes

285. Terpenes in Nature. Terpenes are natural hydrocarbons whose composition corresponds to the formula $C_{10}H_{16}$. Both the terpenes and the related oxygen-containing substances are highly widespread in the vegetable kingdom and are found in what are called essential oils.

The essential oils are contained in various parts of plants: in the roots, the stem, the leaves, the flowers, and the fruits. As a rule, they have a strong and pleasant odour and for this reason have many applications.

Some essential oils, such as lemon, orange, and turpentine oil, are almost exclusively mixture of terpenes.

As far as physical properties are concerned, the terpenes are colourless liquids, which are lighter than water and boil in the 140-190° temperature range. They are highly refractive and are insoluble in water.

An important contribution to elucidating their structure was made by Y. Wagner and his pupils. For many of the terpenes Wagner proposed structural formulas that are universally accepted today.

Much fruitful work in terpene chemistry was also done by S. Namyotkin*.

* Sergei Namyotkin (1876-1950) was born in Kazan. He finished Moscow University and in 1905 began teaching.

Both his M.Sc. and his D.Sc. dissertations were concerned with the nitration of hydrocarbons and the study of dicyclic hydrocarbons by means of this reaction.

Namyotkin began his investigations in the field of the terpenes in 1918 and continued them to the very end of his life. He synthesized and studied many camphene derivatives.

Much of Namyotkin's work was in petroleum chemistry and technology. He contributed to the solution of several problems of petroleum chemistry (the catalytic aromatization of petroleum cuts, the synthesis of chlorine derivatives and alcohols on the basis of petroleum hydrocarbons, the oxidation of paraffins to alcohols and aldehydes, the preparation of detergents, etc.) and wrote a treatise on this section of chemistry.

Several of his papers dealt with the stereochemistry of alicyclic compounds and the synthesis of flavours, herbicides, and plant growth stimulants.

Namyotkin was elected a corresponding member of the U.S.S.R. Academy of Sciences in 1932 and a full member in 1939.

286. Classification of Terpenes. Terpene molecules contain six hydrogen atoms fewer than the molecule of the corresponding saturated hydrocarbon $C_{10}H_{22}$.

Since every double bond, or ring closure, reduces the amount of hydrogen by two atoms, the terpenes may be divided into four groups:

1. Terpenes whose molecules contain an open chain of carbon atoms and three double bonds.

2. Monocyclic terpenes, whose molecules contain a single ring of carbon atoms and two double bonds.

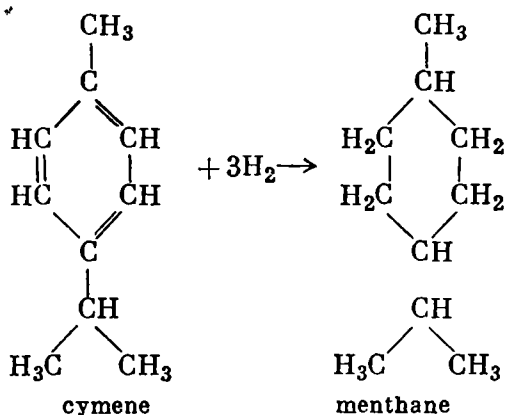
3. Dicyclic terpenes, whose molecules contain two carbon-atom rings and one double bond.

4. Tricyclic terpenes, whose molecules contain no double bonds, while the carbon atoms form three rings.

The most important are the monocyclic and dicyclic terpenes. Most of them are closely related to *p*-methylisopropylbenzene, or cymene.

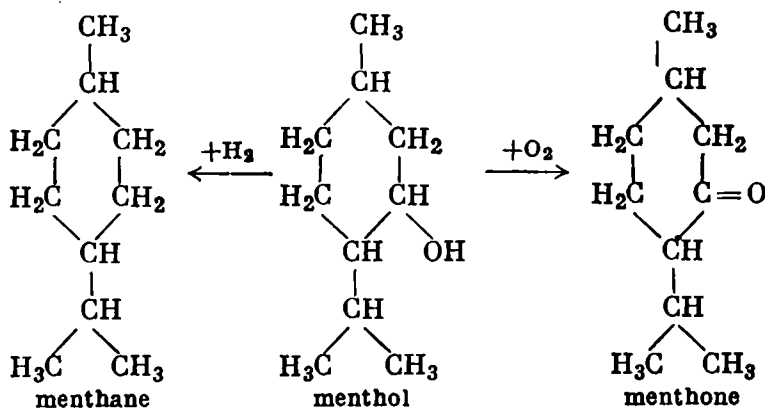
The essential oils, in addition to the terpenes $C_{10}H_{16}$, often contain more complicated hydrocarbons of the same composition, but of higher molecular weight. Their composition can be expressed by the general formula $(C_5H_8)_n$. For terpenes $n = 2$; for polyterpenes n is greater than 2. The polyterpenes are divided into the sesquiterpenes $C_{15}H_{24}$, the diterpenes $C_{20}H_{32}$, etc. The polyterpene derivatives include abietic acid, which is contained in colophony, resin acids, and other natural substances.

287. Monocyclic Terpenes. It will be convenient to begin our survey of the monocyclic terpenes and kindred substances with the hydrocarbon *menthane* $C_{10}H_{20}$, which can be prepared from cymene by adding six hydrogen atoms to its molecule. This is accomplished by leading cymene vapour with hydrogen through a glass tube with finely divided nickel:



Menthane is a liquid, which boils at about 170° . It does not occur in nature, but its alcohol, called *menthol*, is the chief constituent of peppermint oil.

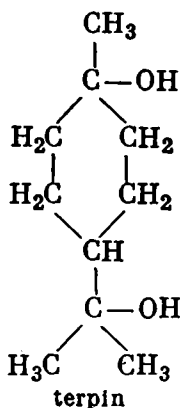
Reduction converts menthol to menthane; consequently, its carbon skeleton is the same:



The properties of menthol as a secondary alcohol are reflected in the fact that its oxidation produces a ketone, *menthone*, which likewise occurs in peppermint oil. Finally, the position of the hydroxyl in its molecule is established by the fact that several reactions convert menthol to *m*-cresol.

Menthol (prismatic crystals) melts at 45° and boils at 212°; it has a strong peppermint odour. It is used in the perfume industry (for tooth-pastes and tooth-powders) and medicinally as an analgesic and anaesthetic during migraine, colds, etc.

The dihydroxy alcohol derived from menthane is called *terpin*. It has the composition $\text{C}_{10}\text{H}_{18}(\text{OH})_2$ and the structure:

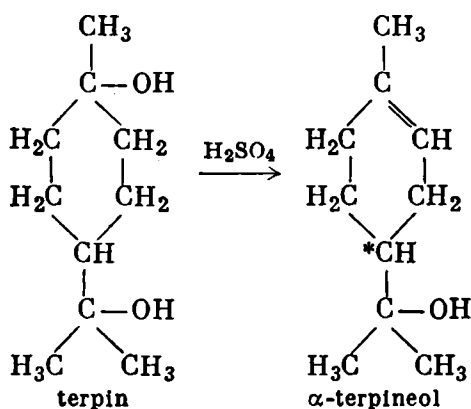


Terpin is a liquid. It can be prepared by treating oil of turpentine with 25% sulphuric acid*.

Treatment with dilute sulphuric acid detaches a molecule of water, producing monohydroxy alcohols with one double bond in the mole-

* The product is the crystalline terpin hydrate $\text{C}_{10}\text{H}_{18}(\text{OH})_2 \cdot \text{H}_2\text{O}$, which gives up the molecule of water of crystallization readily.

cule, such as α -terpineol $C_{10}H_{17}(OH)$:

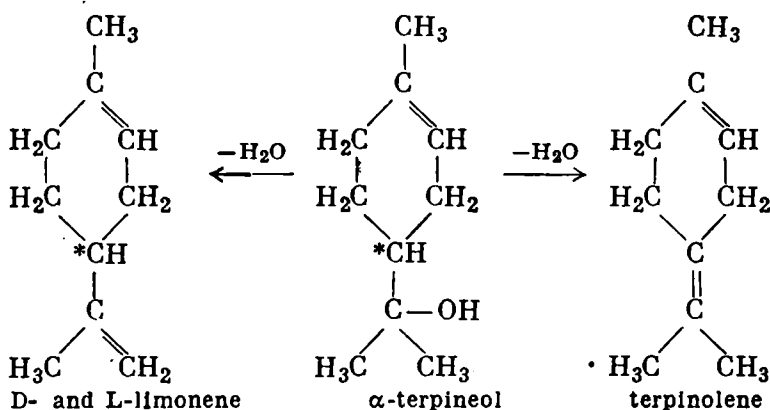


Alpha-terpineol is a crystalline substance (m.p. 38-40°; b.p. 219°) with an odour of lilacs. Optically active modifications are known. The α -terpineol molecule contains an asymmetric atom (designated by an asterisk); it is linked with a hydrogen atom, with

the $-\text{C}(\text{OH})\begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$ group, and with two unequal halves of the ring.

The presence of an asymmetric carbon atom in α -terpineol proves the correctness of the above formula, for if water were given up by the terpin molecule in any other way an asymmetric carbon atom would not be formed.

The removal of a molecule of water from α -terpineol produces terpenes corresponding to the general formula $C_{10}H_{16}$: *terpinolene* (b.p. 185-187°) and *limonene* (b.p. 175°):



In one case the product is a substance whose molecule has an asymmetric carbon atom; in the other case the product is a substance without such an atom. The former formula has been adopted for limonene; the latter, for terpinolene.

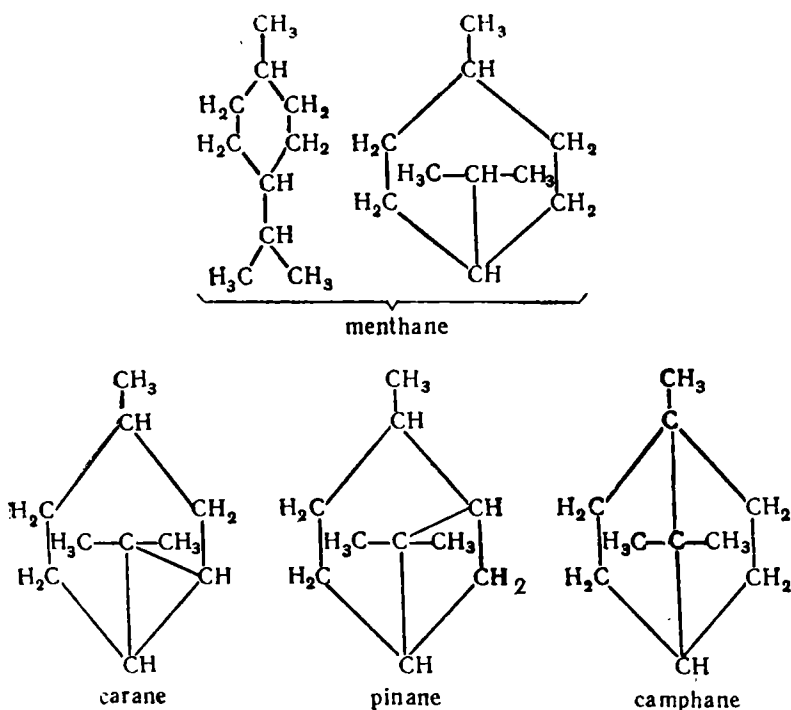
Dextrorotatory limonene accounts for the bulk of the essential oil of the wild orange ring and is the main constituent of lemon, bergamot, caraway, and fennel oils.

Laevorotatory limonene occurs in pine-needle oil. Inactive limonene is known as *dipentene*. It occurs in the essential oil of wormseed and can be obtained by the dry distillation of natural rubber.

Since the limonene molecule contains two double bonds, it can add four halogen atoms or two hydrogen halide molecules.

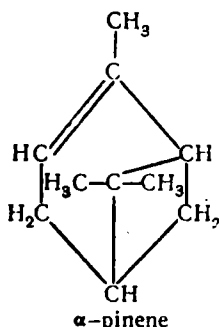
288. Dicyclic Terpenes. Most of the dicyclic terpenes $C_{10}H_{16}$ can be derived from menthane $C_{10}H_{20}$ by closing its second ring and forming a double bond through the removal of two hydrogen atoms. Ring closure produces hydrocarbons of the composition $C_{10}H_{18}$.

Ring closure can be effected by various means. Depending upon the position of the carbon atoms common to both rings, this produces the hydrocarbons *carane*, *pinane*, or *camphane*:



Part of a camphane molecule model is shown in Fig. 73. By removing two hydrogen atoms and forming a double bond in the above dicyclic hydrocarbons, we obtain terpenes corresponding to the general formula $C_{10}H_{16}$.

One such terpene is α -pinene:



Alpha-pinene makes up the bulk of turpentine oil. It is a liquid boiling at 156° . Alpha-pinene is easily oxidized. If, for example, fuming nitric acid is mixed with concentrated H_2SO_4 and the oil of turpentine is added by drops, swift oxidation produces a flash. Alpha-pinene is also oxidized by the oxygen of the air. In this case its molecule adds a molecule of oxygen, forming a substance of the composition $\text{C}_{10}\text{H}_{16}\text{O}_2$. The substance is of the nature of a peroxide and readily oxidizes other substances, giving up an atom of oxygen. That is why in the presence of oil of turpentine the oxygen of the air oxidizes several substances: a solution of indigo becomes colourless, arsenous acid is oxidized to arsenic acid, and the "drying" of varnishes containing unsaturated acids is speeded.

When dry hydrogen chloride is led into cooled oil of turpentine, the product is a compound of pinene and hydrogen chloride $\text{C}_{10}\text{H}_{17}\text{Cl}$, which is very much like camphor in appearance and odour and is for this reason wrongly called artificial camphor. The substance is, however, by no means the same as the camphor prepared synthetically.

Oil of Turpentine. Oil of turpentine is obtained from coniferous trees in the following manner. Part of the bark of a conifer is removed, and an incision is made in the tree-trunk; the resinous exudation solidifies into a viscous mass called turpentine. When this is distilled with steam, the product which collects in the receiver is oil of turpentine; the hard mass remaining in the still is called colophony.

Oil of turpentine is also prepared by the dry distillation of pine stumps. The resin containing oil of turpentine is extracted by various solvents, chiefly petrol with a high boiling point.

Oil of turpentine is used medicinally; in industry it serves to make varnishes and paints.

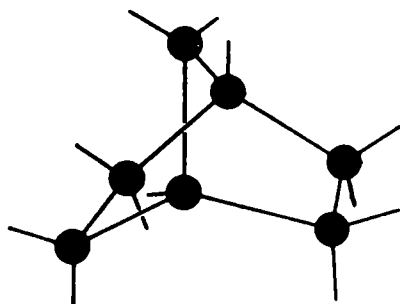


Fig. 73. Part of a camphane molecule model.

Colophony is a mixture of *abietic acid* $C_{20}H_{30}O_2$ (whose molecule contains three six-membered rings) and its anhydride. The alkali salts of this acid have a detergent action; for this reason colophony is often added to the ingredients of certain types of soap with a high foam-forming capacity. It is also used in the production of varnishes and, together with alum, in sizing paper.

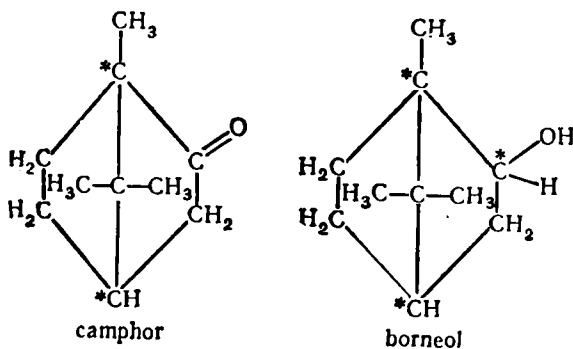
289. Camphor. The most important of the substances related to the terpenes is *Japan* or *laurel camphor* $C_{10}H_{16}O$. It is prepared by distilling the wood and leaves of the camphor laurel with steam.

Camphor crystallizes in glistening prisms; it has a strong characteristic odour, melts at 175° and boils at 209° . Despite its high melting point, camphor sublimes at ordinary temperature.

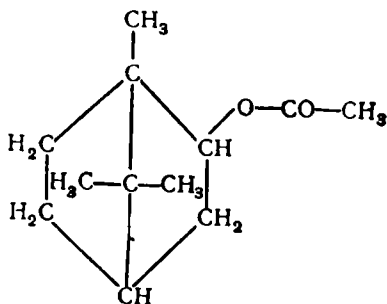
Ordinary natural camphor is optically active, it rotates the plane of polarization to the right: $[\alpha]_D^{20} = +44^\circ$.

Numerous investigations have shown that the structure of camphor corresponds to the formula given below. According to this formula, camphor is a ketone.

The secondary alcohol corresponding to camphor is called borneol (m.p. $202-203^\circ$; b.p. 212°):



Borneol acetate occurs in the needles of the Siberia fir, which is highly widespread in Siberia and in the east of the European part of the U.S.S.R. Its formula is:



The saponification of this ester yields borneol, which can then be oxidized to camphor.

Large amounts of camphor are prepared from turpentine oil. For this purpose α -pinene is by several reactions converted to borneol, which is then oxidized to camphor. In the U.S.S.R. a method of preparing camphor from turpentine oil has been developed and introduced into industry by V. Tishchenko.

The mechanism of the rearrangement of compounds of the pinane and camphane series (the synthesis of camphor from α -pinene) was established by Namyotkin.

Camphor is used medicinally; large amounts of it are also used in making celluloid and smokeless powder.

Carotenoids

The carotenoids are natural coloured substances similar in structure to carotene, the yellow-red pigment of carrots. Carotenoid molecules contain a large number of conjugated double bonds. These substances are polyene pigments. Carotenoids are soluble in animal and plant fats; they have characteristic absorption spectra and give an indigo blue colour with strong sulphuric acid. Most of them are easily oxidized by the oxygen of the air.

290. Lycopene. This hydrocarbon, with the composition $C_{40}H_{56}$, is largely responsible for the colour of tomatoes and of the haws of the wild rose. Lycopene forms carmine prisms (m.p. $168-169^\circ$). Its molecule contains thirteen double bonds. When treated with hydrogen in the presence of catalysts, it adds 26 atoms of hydrogen per molecule to become the saturated hydrocarbon $C_{40}H_{82}$. A study of lycopene decomposition reactions leads to the assumption that it has the formula shown on p. 521. According to this formula, the carbon atom sequence typical of the isoprene carbon skeleton recurs in the lycopene molecule eight times; moreover, the recurring groups (separated in the formula by dotted lines) are not all linked identically: in the middle of the molecule they are rearranged, owing to which the molecule appears to be made up of two equal and symmetrically arranged parts.

291. Carotene. Carotene $C_{40}H_{56}$ is isomeric with lycopene. It occurs in carrots, in many flowers, in fruit, milk, and blood serum. Together with its dihydroxy derivative yellow *xanthophyll* $C_{40}H_{54}(OH)_2$, it is contained in green leaves and accounts for their autumn colour. Three isomers of carotene are known: β -carotene (m.p. 183°), α -carotene (m.p. 187°), and γ -carotene (m.p. 178°).

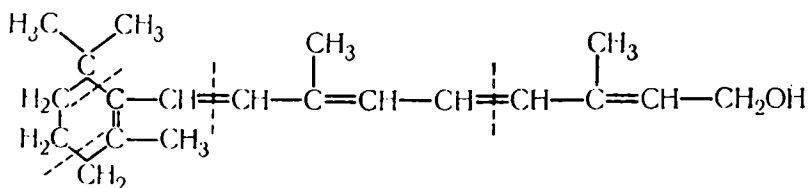
A study of the decomposition products of β -carotene suggests that its structure is that represented on p. 521.

The formula of α -carotene may be derived from the formula of lycopene by ring closure at both ends of the carbon chain; this occurs at the tenth carbon atoms from the middle of the molecule.

The structure of α -carotene (p. 521) differs from the structure of β -carotene only in the position of the double bond in one of the rings.

Gamma-carotene is in structure intermediate between β -carotene and lycopene: one half of its molecule is similar to half of a β -carotene molecule, while the other half is similar to half of a lycopene molecule (i.e., the γ -carotene molecule contains only one ring).

292. Vitamin A. Vitamin A is very similar in structure to β -carotene. It is a light yellow oil, whose composition is $C_{20}H_{29}OH$. It is soluble in fats and can be distilled in a high vacuum. The structure of this vitamin corresponds to the formula:



A comparison of this formula and that of β -carotene reveals that the vitamin A molecule corresponds to half of the β -carotene molecule, a hydroxyl and a hydrogen atom being added at the point of rupture.

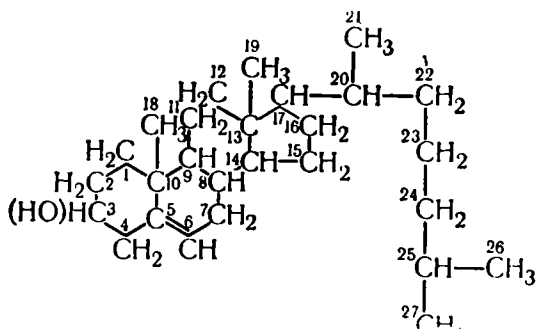
Vitamin A is found in milk (especially in summer, when cows feed on fresh grass); in butter, in egg yolk, in cod-liver oil, and in most vegetables and fruits. It is a growth factor, and its deficiency in the human diet causes loss of weight, a drying of the retina of the eye, and a decline in resistance to infection.

Carotene can serve as a substitute for vitamin A, as it is a vitamin A precursor: in the animal organism it is converted to vitamin A, which is often stored in considerable quantities in the liver.

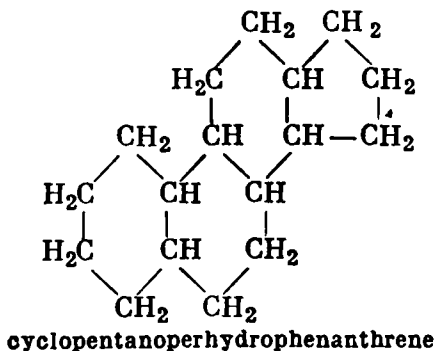
Sterols, Bile Acids, and Steroid Hormones

293. Sterols. The sterols are a group of monohydroxy polycyclic alcohols that are highly widespread both in the animal and the plant kingdom. Their molecules contain four carbon rings, three of which are six-membered, but are not aromatic.

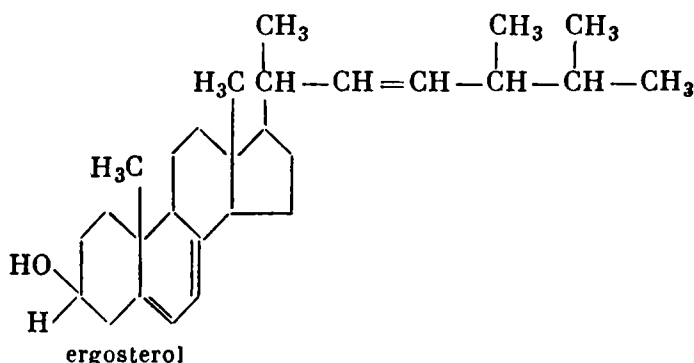
The sterol that has been known for the longest time is cholesterol (from the Greek *chole* meaning bile and *stereos* meaning solid) $C_{27}H_{45}OH$. It is found—partly in ester form—in nearly all the organs of the human body; it is present in especially large quantities in the brain and the nerve substance. Cholesterol was first isolated from gall-stones, of which it is the main constituent. It is a crystalline substance (m.p. 149°); its structure was established in 1932, chiefly by the work of Wieland and Windaus:



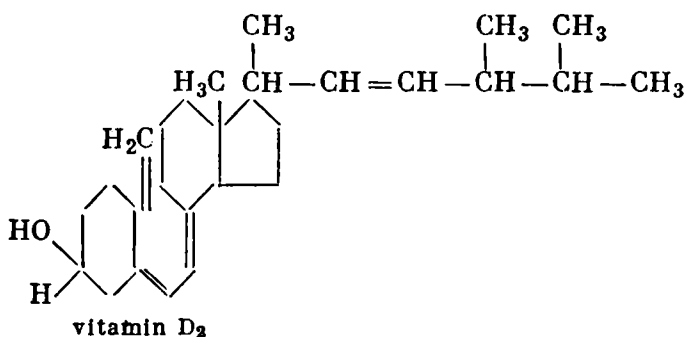
It is evident from this formula that cholesterol is a secondary alcohol; its molecule contains the hydrogenated phenanthrene system condensed with the cyclopentane ring. Like cholesterol, the other sterols also have the *cyclopentanoperhydrophenanthrene* skeleton in their molecules:



A typical mycosterol (sterol found in yeasts and fungi) is *ergosterol* $C_{28}H_{43}OH$ (m.p. 163°):



Ergosterol can be isolated from yeast and certain other products. Exposure to ultraviolet light ruptures one of the six-membered rings in its molecule. This produces a substance similar in action to the anti-rickets vitamin contained in cod-liver oil. The substance has been named *vitamin D₂*; the commercial product is called *calciferol* (m.p. $115-117^\circ$). It has the structure:



Very many natural substances are known whose molecules, like those of the sterols, contain the cyclopentanoperhydrophenanthrene skeleton. These include the bile acids, sex hormones, cardiac poisons from the leaves, seeds, and roots of the foxglove (*Digitalis*) and from varieties of the plant *Strophanthus*, to name only a few substances. The whole group have come to be known as the *steroids*.

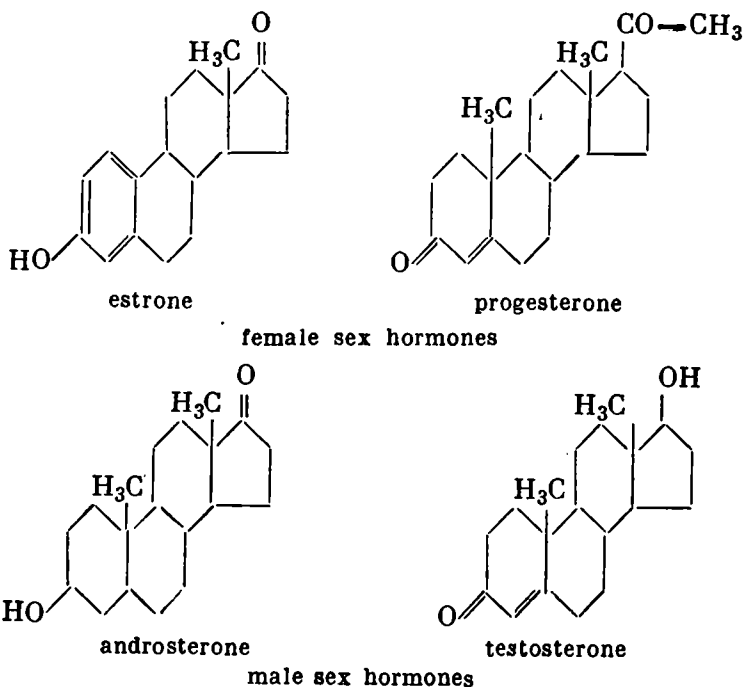
294. Bile Acids. Bile acids are found in the bile of human beings and many animals. The human bile, for instance, contains:

<i>cholic acid</i>	$C_{23}H_{36}(OH)_3COOH$
<i>desoxycholic acid</i>	$C_{23}H_{37}(OH)_2COOH$
<i>anthropodesoxycholic acid</i>	$C_{23}H_{37}(OH)_2COOH$
<i>lithocholic acid</i>	$C_{23}H_{38}(OH)COOH$

295. Steroid Hormones. The steroid hormones are secreted by the sexual glands and the adrenal cortex. In the organism they play an extremely important role, regulating the processes of metabolism, growth, reproduction, and ageing.

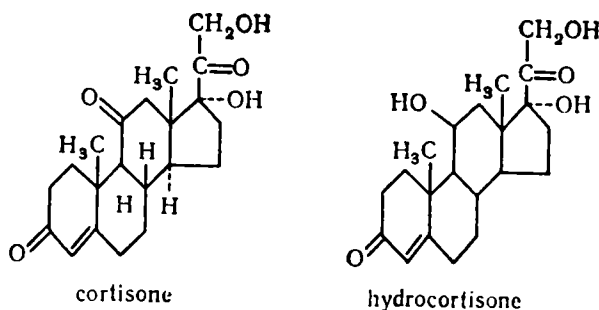
According to their biological action, the steroid hormones are divided into the sex and corticoid hormones. Sex hormones are secreted by the sexual glands and are responsible for the development of specific male and female sexual characteristics.

The following are examples of sex hormones:



If the COCH_3 in the female sex hormone progesterone is replaced by a hydroxyl, we obtain the structural formula of the male sex hormone testosterone.

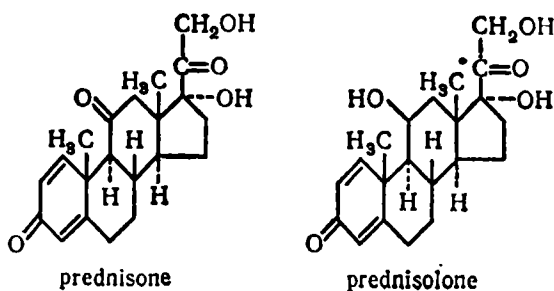
Corticoid Hormones. The most important corticoid hormones are *cortisone* and *hydrocortisone*:



In medicine the corticoid hormones are used primarily to treat ailments of the adrenal glands. They are also used extensively in the treatment of rheumatic ailments, inflammatory conditions, bronchial asthma, and quite a number of other diseases.

It has lately been established that the introduction of a double bond into the 1-2 position of cortisone and hydrocortisone considerably enhances their activity.

This has led to the synthesis of the new medicines *prednisone* and *prednisolone*:



Part Three

HETEROCYCLIC COMPOUNDS

CLASSIFICATION AND GENERAL CHARACTERISTICS

296. Classification and General Characteristics of Heterocyclic Compounds. In the previous parts of the book we have considered compounds with an open chain of carbon atoms (the so-called acyclic compounds) and compounds whose molecules contain cycles of carbon atoms (carbocyclic compounds). The present part deals with heterocyclic compounds (or heterocycles). *The molecules of the heterocyclic compounds contain cyclic groups that, in addition to carbon atoms, have other (hetero) atoms in them.* As among carbocyclic compounds, the most common among the heterocyclic compounds are those with five- and six-membered cycles. The stability of these cycles and the readiness with which they form is due to the absence of strain in them (p. 508). Heterocyclic compounds can form systems of two and more cycles, for example, through coupling with aromatic rings.

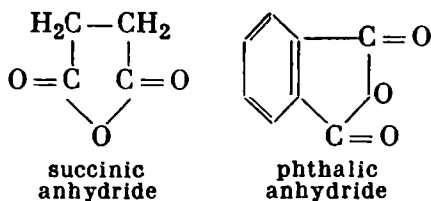
The reason why heterocyclic compounds are considered in the last part of the book is that their structure is more complex than the structure of either the aliphatic or the aromatic compounds. Consequently, their chemical properties and reactions are likewise more complex.

The heterocyclic compounds are very important both in nature and industrially. This class of compounds includes such important natural substances as the chlorophyll of plants, the haemin of the blood, heteroauxin, indigo, and penicillin, to name only a few. The poisons of vegetable origin known as the *alkaloids* (quinine, morphine, nicotine, etc.) are another extremely large group of heterocyclic compounds.

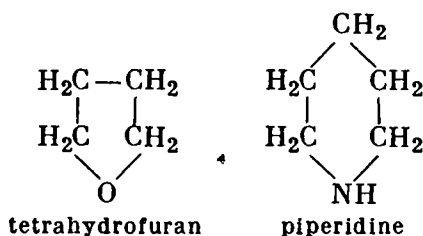
The heterocyclic compounds also include such most important groups as the so-called vat and sulphur dyes, as well as a very large number of diverse drugs: sulphapyridine, sulphazole, synthetic anti-malarial drugs (atebrin and plasmoquin), and many others.

The physical and, especially, the chemical properties of the heterocyclic compounds are largely determined by the nature of the linkages in the cycle. Substances without double bonds in the cycle are as a rule like acyclic and alicyclic compounds.

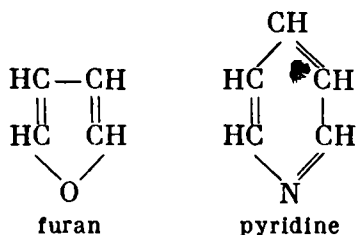
For example, formally succinic anhydride and phthalic anhydride



should be referred to the heterocyclic compounds. In chemical properties, however, they do not differ substantially from ordinary anhydrides, except perhaps in the readiness with which they form. Similarly, a compound like tetrahydrofuran exhibits all the properties of an ordinary ether, while piperidine exhibits the properties of an ordinary secondary aliphatic amine:



Certain specific properties of heterocyclic compounds are brought out by a conjugated system of double bonds in the cycle, as in furan and pyridine:

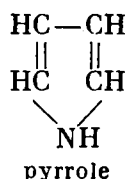
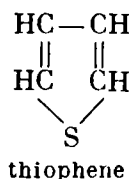
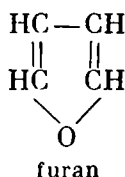


Such compounds display a somewhat aromatic character. When treated with halogens, nitric and sulphuric acids, and other similar reagents, heterocyclic compounds with conjugated double bonds undergo reactions of substitution rather than addition.

The nomenclature of the heterocyclic compounds is like that of the aromatic compounds. The name of the heterocycle serves as the root of the word, while the substituents are named in the same order as in aromatic compounds. For example, the OH group in the cycle is called hydroxy, while compounds containing the COOH group are called carboxylic acids. The position of an atom or group in the cycle is designated by a number, with the numbering as a rule beginning from the hetero-atom. If the compound has several hetero-atoms, the numbering begins with the oxygen atom, it being followed by the atom of sulphur and then nitrogen.

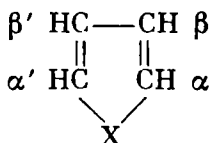
Five-Membered Heterocyclic Compounds

297. General Characteristics of Five-Membered Heterocyclic Compounds. The main groups of heterocyclic compounds with a five-membered cycle are the groups of furan, thiophene, and pyrrole:

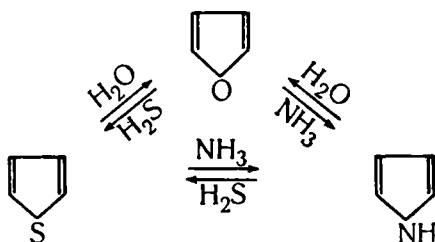


The three parent substances of these groups are similar in structure and in a number of properties.

If we denote the hetero-atom with the letter X, the general formula of these compounds can be written as follows:

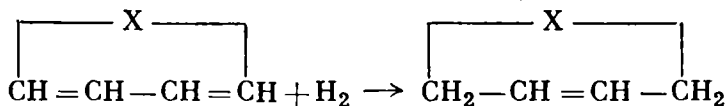


The close relationship between furan, thiophene, and pyrrole is borne out most strikingly by the fact that they can be transformed into one another. It has been shown by Y. Yuryev that when furan vapour mixed with hydrogen sulphide or ammonia is led over Al_2O_3 at $400\text{--}500^\circ$, the following mutual transformations take place:

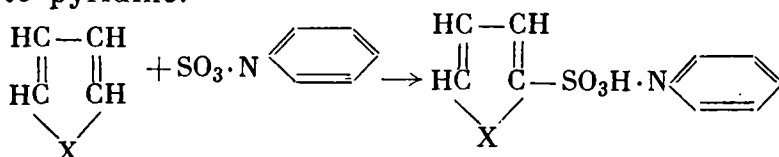


Furan, thiophene, and pyrrole have a system of conjugated double bonds and, in their behaviour in several reactions, closely resemble unsaturated compounds of the divinyl type (resinification by acids, polymerization, etc.). On the other hand, they also resemble

aromatic compounds (replacement of hydrogen atoms by halogenation, nitration, sulphonation, and acylation). Such typical reactions as hydrogenation proceed along the same lines as in the case of divinyl (the hydrogen first assumes positions 1 and 4):

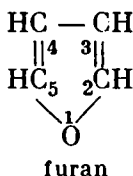


The reactions characteristic of aromatic compounds (sulphonation-nitration, and acylation) proceed with the replacement of the α -hydrogen atoms. This is illustrated by the sulphonation reaction. As demonstrated by A. Terentyev, this reaction can be effected with furan, thiophene, pyrrole, and several of their homologues by heating the compound with the product of the addition of sulphur trioxide to pyridine:



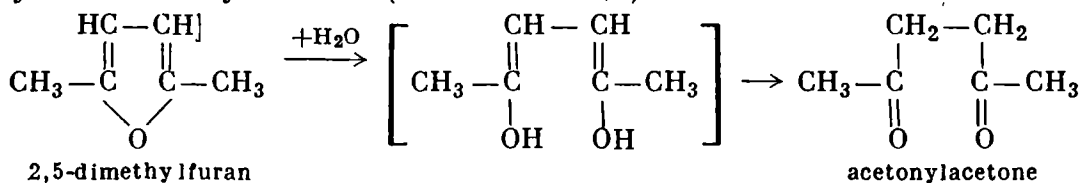
FURAN GROUP

298. Furan. Furan is a liquid, which is slightly soluble in water (b.p. 32°)

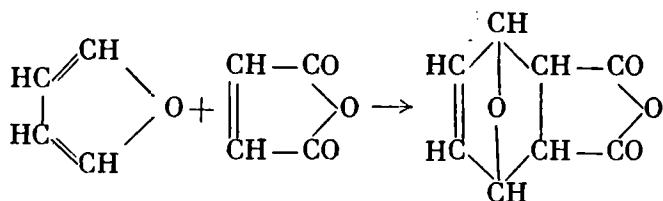


When a splint of wood dipped in hydrochloric acid is exposed to the vapours of furan, a green colour is produced on the splint. Furan, as well as its closest homologues α -methyلفuran (silvan) and α,α' -dimethyلفuran, occurs in the highly volatile fractions of the destructive distillation of wood. Pure furan is usually prepared by heating pyromucic acid (p. 536) with diphenylamine.

In structure and properties furan somewhat resembles vinyl alcohol ethers. Like them, furan and its homologues are resistant to the action of alkalis, but are hydrolyzed by heating with dilute hydrochloric acid. Furan in this case yields succindialdehyde, which undergoes transformations very readily, while 2,5-dimethyلفuran yields acetonylacetone (hexandione-2,5):



The diene character of furan is illustrated by the fact that it is resinified by sulphuric acid. Oxidizing agents (nitric acid) convert it to maleic acid. Hydrogenation turns furan first into 2,5-dehydrofuran and then into tetrahydrofuran. The latter is like a typical ether in character. Like divinyl (p. 94), furan is easily added to maleic anhydride:



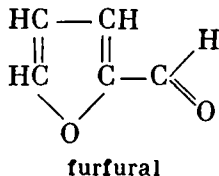
The aromatic character of furan is reflected in its behaviour upon halogenation, nitration, and sulphonation.

The chlorination of furan with sulphuryl chloride produces 2-chlorofuran, a liquid boiling at 77°. When furan is treated with nitric acid in a solution of acetic anhydride, the product is 2-nitrofuran, the yield being poor. The sulphonation of furan produces furansulphonic-2 acid, while acetylation by acetic anhydride in the presence of zinc chloride (Y. Goldfarb and L. Smorgonsky) yields 2-acetylfuran and 2,5-diacetylfuran.

Substituents of the first class (OH, NH₂) enhance the reactivity of the benzene ring and thereby make it less stable. They have the same effect on the furan nucleus, and it is not surprising therefore that the hydroxy and amino furans are difficult to obtain (owing to their instability). Substituents of the second class, just as in the aromatic division, make the furan nucleus less reactive. For this reason the aldehydes, ketones, and acids of furan are far less stable than furan itself or its homologues.

The best known derivatives of furan are furfural and pyromucic acid.

299. Furfural. Furfural is a colourless liquid boiling at 162°; it darkens easily and is resinified upon standing, due to the action of the air. As is evident from its name, furfural is an aldehyde:

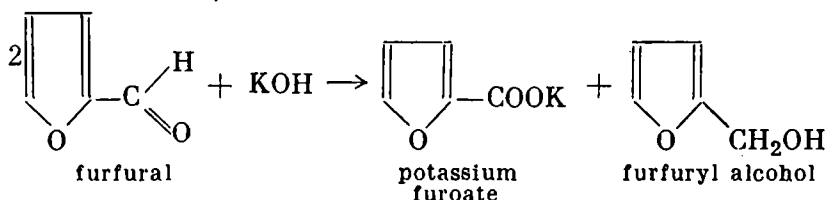


Its odour is reminiscent of freshly baked bread.

Furfural can be prepared by heating with dilute acids such cereal hulls as contain pentoses (p. 304). Other materials from which it can be prepared are bran (A. Engelhardt, 1870), sunflower seedhusks, etc.

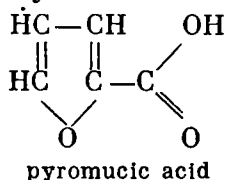
The reactivity of the hydrogen atoms in the furfural cycle is weakened by the aldehyde group. This makes the chemical properties of furfural very similar to those of benzaldehyde.

Oxidizing agents (KMnO_4) turn furfural into furancarboxylic (pyromucic) acid. Treatment with strong alkalis converts furfural, by virtue of the Cannizzaro-Tishchenko reaction, to an equimolecular mixture of pyromucic acid and furfuryl alcohol.



Very small quantities of furfural can be detected in a mixture by treating it first with acetone and then with strong sulphuric acid; this produces a deep crimson colour (V. Chelintsev). The reaction can also be used for detecting acetone. An equally sensitive test consists in heating furfural with aniline acetate; this produces a red colour.

300. Pyromucic Acid. Pyromucic acid



is usually prepared from furfural, but it can also be obtained by heating mucic acid or saccharic acid. It forms colourless crystals (m.p. 130°) and is a stronger acid than benzoic acid.

When heated, pyromucic acid gives up CO_2 and turns into furan.

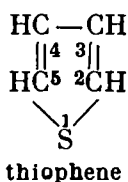
The carboxyl in the furan cycle of pyromucic acid lends it considerable stability.

In an anhydrous medium pyromucic acid undergoes chlorination, bromination, nitration, and sulphonation, primarily in α -position.

Furan and its derivatives, although readily available, have so far found little industrial application.

THIOPHENE GROUP

301. Thiophene. Thiophene is a colourless liquid boiling at 84° :

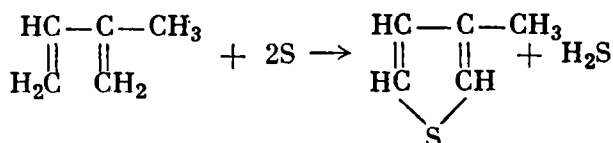


It has a characteristic odour resembling that of crude paraffin oil.

The discovery of thiophene took place in interesting circumstances. In 1883 the German chemist V. Meyer was demonstrating the preparation of benzene by distilling sodium benzoate with soda lime at a lecture and carried out what was believed to be a qualitative test for benzene. This consisted in treating benzene with a solution of isatin in concentrated sulphuric acid; the appearance of a blue colour was thought to indicate the presence of benzene. But in this case the experiment was unsuccessful. The reagent was tested with ordinary grades of benzene, and everything proceeded normally. Curious about this phenomenon, Meyer staged several experiments and soon established that the colour was due not to benzene itself, but to an impurity that is contained in a small amount in coal-tar benzene and is difficult to separate from it. An investigation of this impurity disclosed that it is a sulphur-containing compound C_4H_4S , very similar in properties to benzene. This prompted Meyer to name it thiophene.

Thiophene compounds occur in coal-tar. The sulphur-containing compounds present in petroleum likewise partly consist of thiophene homologues.

Good yields of thiophene are obtained by the Yuryev reaction: the passage of furan vapour and hydrogen sulphide over aluminium trioxide at 450° . Thiophenes are also formed when divinyl or isoprene is led into the vapour of boiling sulphur:



Thiophene is stable to heating. In many of its properties it is very similar to benzene, but differs from it in the relative readiness with which it undergoes oxidation by hypochloric acid, nitric acid, etc. In this respect thiophene resembles furan compounds. The aromatic character of thiophene is evidenced by various substitution reactions. With certain precautions (dilution with inert solvents, cooling), chlorine and bromine treatment yields α -halogen derivatives of thiophene. Similarly, nitration and sulphonation in mild conditions produces α -nitrothiophene and α -sulphothiophene respectively.

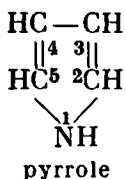
Thiophene is more reactive than benzene; this distinction is utilized to remove traces of thiophene from benzene.

To purify crude benzene, it is shaken with a small quantity of 85% sulphuric acid, which extracts the thiophene as sulphothiophene.

The reduction of α -nitrothiophene yields α -aminothiophene, which has properties similar to those of aniline. Unlike aniline, however, it does not react with nitrous acid to form diazo-compounds, but undergoes profound oxidation.

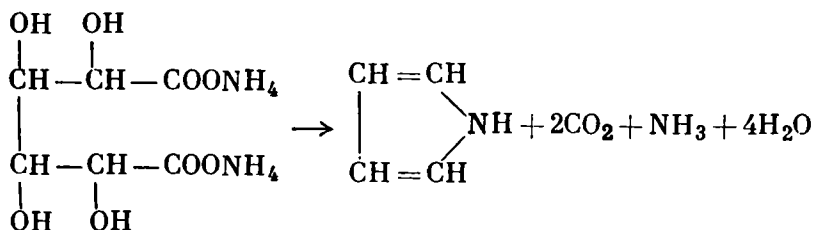
PYRROLE GROUP

302. Pyrrole. Pyrrole is a liquid (b.p. 131°), which is slightly soluble in water



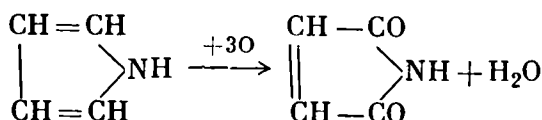
Pyrrole was first found in coal-tar and in bone oil, the oil obtained by the destructive distillation of bones. It derives its name (the Greek word *pyrrhos* means fiery) from the fact that its vapour imparts a red colour to a splint moistened with hydrochloric acid.

Pyrrole can be isolated from bone oil. It can also be prepared by Y. Yuryev's method (p. 533) by treating furan with ammonia. If methylamine or aniline is taken instead of ammonia, the product is 1-methyl- or 1-phenylpyrrole respectively. Pyrrole is also formed when ammonium saccharate is heated in glycerol (Y. Khotinsky):



The presence of the NH group identifies pyrrole as a secondary amine. Pyrrole reacts with metallic potassium to form potassium pyrrole. Treatment with methyl iodide turns potassium pyrrole into 1-methylpyrrole, while treatment with acetic anhydride converts it to 1-acetylpyrrole. The basic properties of the NH group are very faintly pronounced.

The diene character of pyrrole is even more marked than that of furan. In the presence of even a small amount of mineral acid, pyrrole most readily turns into a dark red resin, a mixture of polymers. When stored, especially upon exposure to light and air, it quickly resinifies. The action of oxidizing agents (nitric acid, chromic acid, etc.) easily converts it to *maleimide*:



Pyrrole is quite resistant to alkalis.

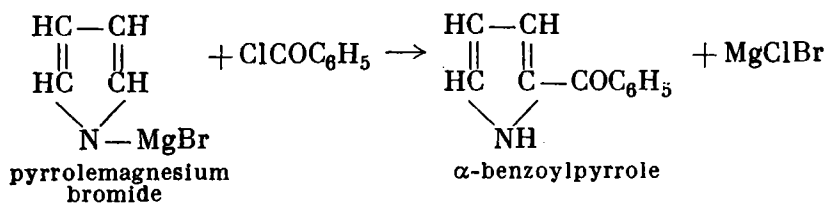
Like furan, pyrrole exhibits an aromatic character; the readiness with which it reacts often resembles that of phenol. When, for example, pyrrole is treated with iodine in an aqueous solution of an alkali, tetraiodopyrrole forms readily. This substance is known as *iodol*. Chlorine and bromine in similar conditions oxidize pyrrole.

Ordinary nitration with nitric acid completely destroys the pyrrole ring. Concentrated sulphuric acid causes intense resinification of pyrrole. The treatment of pyrrole with the product of the addition of sulphur trioxide to pyridine gives quantitative yields of α -pyrrole *sulphonic acid*. Its salts are quite stable compounds.

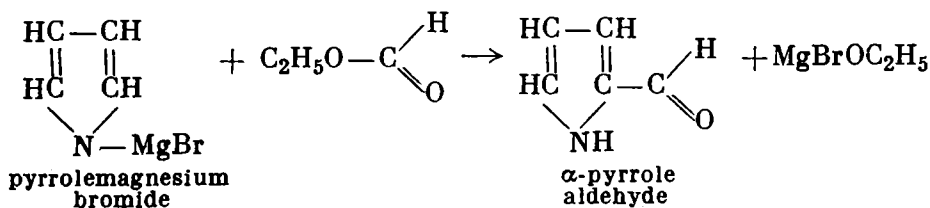
The carboxyl is introduced into the pyrrole ring by treating potassium pyrrole with carbon dioxide. This at first produces a salt of N-pyrrolecarboxylic acid and, at 200°, a salt of α -pyrrolecarboxylic acid. The reaction is similar to that whereby salicylic acid is prepared from sodium phenolate (p. 441).

Another reaction that proceeds similarly is the preparation of mixed organomagnesium derivatives of pyrrole, e.g., by treatment with ethylmagnesium bromide. The reaction product, without any considerable heating, yields α -pyrrolecarboxylic acid.

When pyrrolemagnesium bromide is treated with acid chlorides and anhydrides or esters, the products are ketones. When, for instance, pyrrolemagnesium bromide reacts with benzoyl chloride, the product is α -benzoylpyrrole (m.p. 79°):

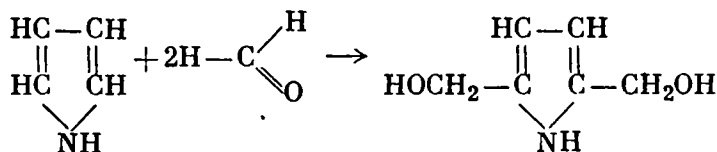


The interaction of pyrrolemagnesium bromide with a formic acid ester produces α -pyrrole aldehyde (V. Chelintsev and A. Terentyev), a solid melting at 50°:

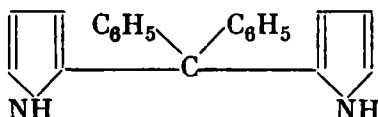


Aldehydes and ketones condense readily with pyrrole, the α -hydrogen atoms participating in the condensation. When, for instance, pyrrole reacts with formaldehyde in the presence of an alkali, the

product is a dihydroxy alcohol (A. Chelintsev and B. Maksorov):



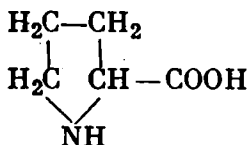
The action of fatty and aromatic ketones on pyrrole has been studied in great detail, and it has been shown that condensation products are formed primarily.



The most reactive hydrogen atoms in unsubstituted pyrrole are thus the α -atoms. The pyrrole derivatives, in their stability, may be divided into two groups. Derivatives with substituents of the first class, i.e., homologues and hydroxy- and amino-derivatives, in which $-\text{OH}$ and $-\text{NH}_2$ groups are attached to pyrrole ring carbon atoms, are less stable. The more stable compounds are derivatives with substituents of the second class: $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{CHO}$, $-\text{COCH}_3$, etc. This is the same picture that we observed in the case of the aromatic compounds and the furan derivatives.

Compounds containing the pyrrole ring occur extensively in the animal and plant kingdoms.

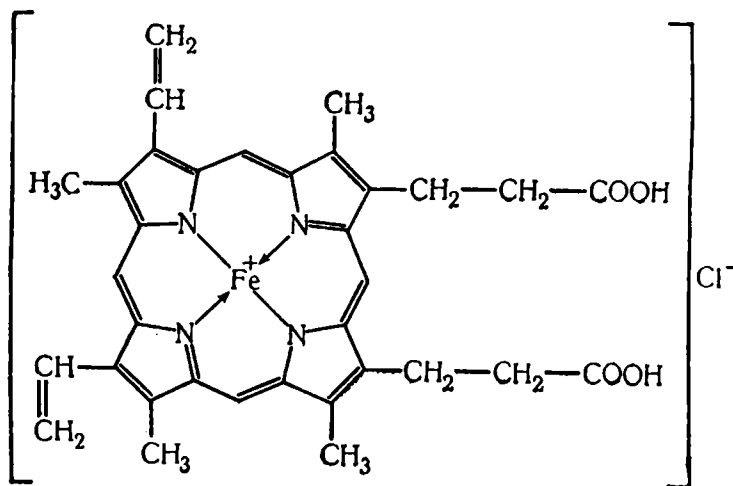
303. Pyrrolidine. Reduction causes the pyrrole molecule to add two hydrogen atoms (in positions 2 and 5), forming dihydropyrrole, or *pyrroline*. Further hydrogenation produces tetrahydropyrrole, or *pyrrolidine*. This compound is similar in properties to secondary aliphatic amines. It is a liquid (b.p. 88.5°) with the characteristic odour of ammonia; upon exposure to air, it fumes greatly. Among the derivatives of pyrrolidine, mention should be made of α -pyrrolidinecarboxylic acid, or *proline*:



This is one of the amino acids formed in protein hydrolysis.

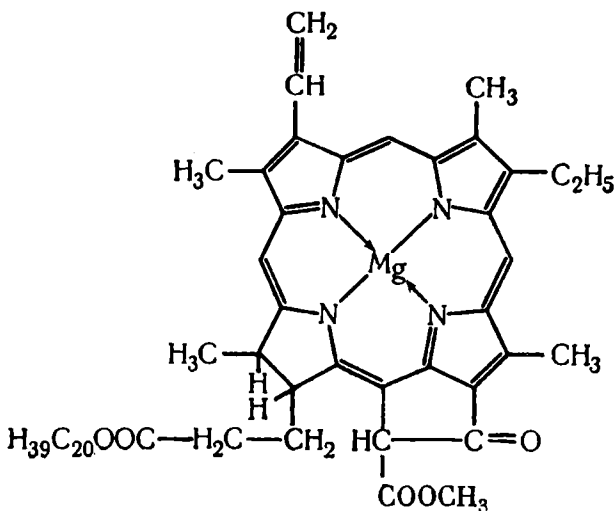
304. Haemin and Chlorophyll. Particularly important derivatives of pyrrole are the pigments of the blood and of green plants. The colouring matter of the blood, haemoglobin, which plays the part of an oxygen carrier, is a complex protein. Hydrolysis breaks it up into the protein *globin* and the non-protein *haemin*. The haemin molecule

contains four pyrrole rings linked by methine ($\text{CH}=\text{}$) groups. An essential part of the haemin molecule is the coordinately linked iron atom:



Chlorophyll, the green pigment of the leaves, consists of two substances of similar structure: blue-green chlorophyll *a* and yellowish green chlorophyll *b*. The role of chlorophyll was established largely by the work of K. Timiryazev. The separation of the two pigments, which are very similar in properties, was first accomplished by another Russian botanist, M. Tsvet, who employed a method of his invention for this purpose (p. 542).

The chlorophylls are structurally very similar to haemin. Like the haemin molecule, their molecules have four pyrrole rings and a metal atom (whereas in haemin it is iron, in the chlorophylls it is magnesium). Chlorophyll *a* is believed to have the following structure:



By treating each section with a solvent (petrol or benzene with the addition of alcohol), it is possible to achieve the complete extraction of the pigments for subsequent investigation.

The Tsvet method is used extensively to separate mixtures of substances that cannot be separated by other techniques. By means of this technique it has been possible to isolate and study various substances that occur in plants and animal organisms in very small quantities: pigments of fruits and flowers, vitamins, pigments of butterfly wings (pterins), alkaloids, and many others.

Chromatographic methods of analysis based on the different adsorptive capacity of individual chemical substances have become very widespread in the laboratory and in industry for the rapid and accurate determination of the composition of multicomponent fluid mixtures of compounds of similar physical and chemical properties. The instruments specially designed for this purpose are called *chromatographs*.

In industry chromatographic techniques are used to isolate and purify various products.

In the laboratory the method of *rising chromatography on paper* is widely used.

A strip of special chromatographic paper 40-60 cm long is used for the test. A drop of the mixture to be analyzed (0.5-1 mg/ml concentration) is deposited by means of a capillary pipette on the bottom part of the strip. After drying, the strip is hung in a special chamber (Fig. 75) in such a way that its end should be dipped into a solvent at the bottom (for example, a mixture of butyl alcohol, water, and acetic acid is used for amino acids). When the solvent has risen almost to the top of the strip, it is removed and the upper boundary of the solvent (the front) is marked with a pencil. The chromatogram is now dried and developed by spraying with a specially chosen indicator from an atomizer. This produces coloured stains characteristic of each component of the mixture (Fig. 76). If the mixture consists of coloured components, characteristic coloured stains appear on the chromatogram at

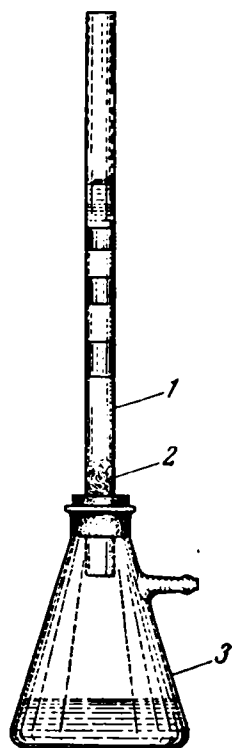


Fig. 74. Apparatus for chromatographic analysis:

1 — chromatographic column with coloured bands of sorbent; 2—mesh and layer of cotton wool; 3—suction bottle.

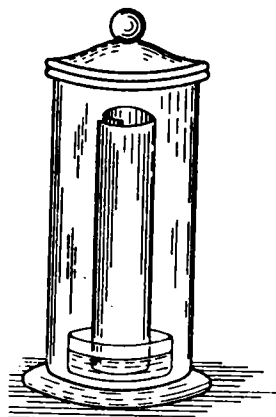


Fig. 75. Chamber for paper chromatography.

once and no development is required.

The identification of the components on the chromatogram is based on the fact that individual substances have definite coefficients of distribution R_f in corresponding systems of solvents. The value of R_f

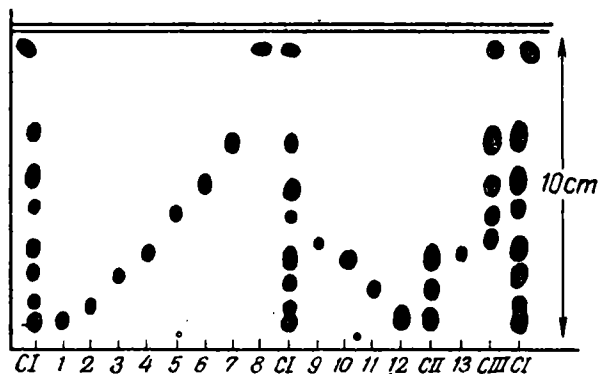


Fig. 76. A paper chromatogram for sugars.

is determined by measuring the distance x from the line where the substance was deposited on the paper (start) to the centre of the stain and the distance y from the start line to the front line of the solvent (Fig. 77). The value of R_f is then calculated according to the formula:

$$R_f = \frac{x}{y}$$

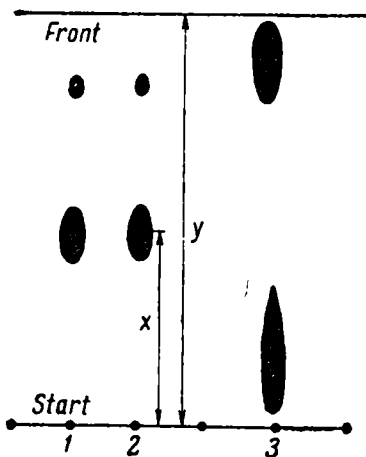


Fig. 77. Determination of R_f in paper chromatography.

In the tables of R_f values for individual substances we then find what substance corresponds to the obtained value of R_f .

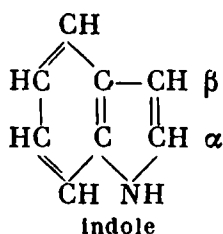
Since the R_f value is affected by many factors (solvent, temperature, etc.), blank tests are often made in chromatographic analysis. For this purpose, one or several drops of pure substances in solution are deposited on the same start line at a distance of 3-4 cm from the test drop. The pure substances chosen are substances suspected of being components of the mixture that is being analyzed. The position of the resulting stains on the developed chromatogram is then compared. Chromatography on paper usually takes 12-18 hours.

A more convenient and quicker technique is "thin-layer" chromatography. In this case a powdered sorbent, such as specially prepared alumina, is deposited evenly on a plate (Fig. 78); a drop of the solution of the mixture to be analyzed is then deposited on the start line.

After the distribution of the components of the mixture in the sorbent layer and their separation, the chromatogram is developed by a suitable reagent, which forms a coloured compound with the substance that is being analyzed (iodine vapour is most frequently used for this purpose). Chromatography by this technique can be accomplished in 15-20 minutes.

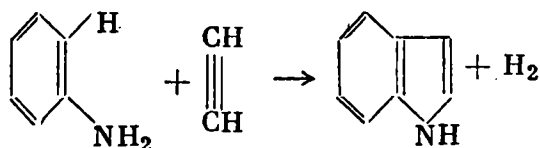
INDOLE GROUP

306. Indole. Indole is a colourless solid melting at 52.5° and boiling at 254° :



It is an ingredient of the essential oils of certain flowers (jasmine) and is formed in appreciable quantities during the putrefaction of proteins and the destructive distillation of coal; it can also be isolated from some of the fractions of coke-oven tar. Purified indole is used in the perfume industry, for it imparts a characteristic pleasing odour to a mixture of fragrant substances; the substance itself, however, in the pure state has a strong odour of faeces.

Structurally the pyrrole ring of indole is condensed with a benzene ring, just as two benzene rings are condensed in naphthalene. The presence of a benzene ring in the molecules of indole compounds is confirmed by the methods of their preparation. Indole, for instance, can be prepared (A. Chichibabin) by leading aniline vapour and acetylene through a tube heated to $600-700^\circ$:



The yield can be increased by diluting the reaction mixture with carbon dioxide. The indole homologues are usually prepared from the phenylhydrazones of aldehydes or ketones by heating them with zinc chloride (E. Fischer) or with cupric chloride (A. Arbuzov). The phenylhydrazone of acetone in this case yields α -methylindole, while

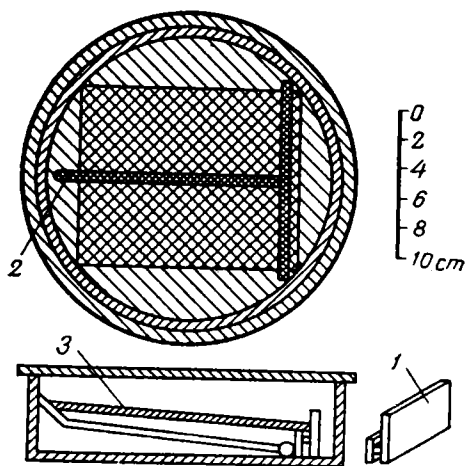
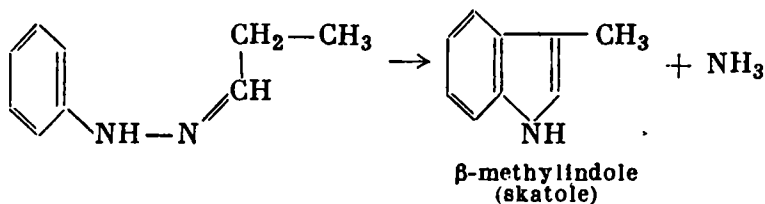


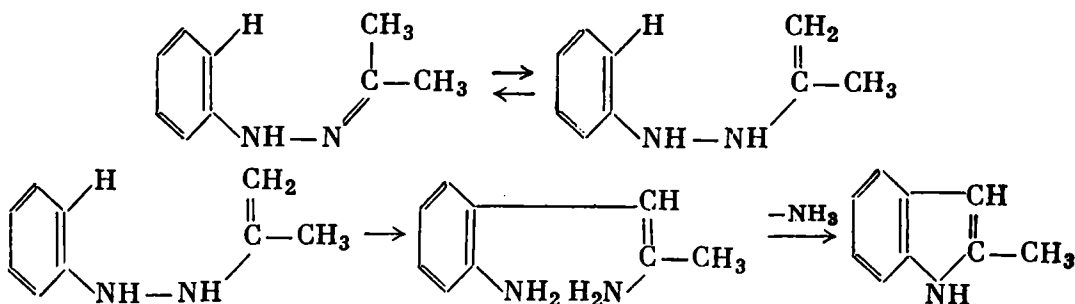
Fig. 78. Apparatus for "thin-layer" chromatography:

1—plate on which a sorbent is evenly distributed; 2—plate holder; 3—chromatogram to be developed in a closed vessel.

the phenylhydrazone of propionaldehyde yields β -methylindole:



The process evidently proceeds through the formation of a tautomeric unstable intermediate with a structure and properties similar to those of hydrazobenzene. The reaction (for the phenylhydrazone of acetone) should in that case, as in the formation of benzidine, follow these stages:



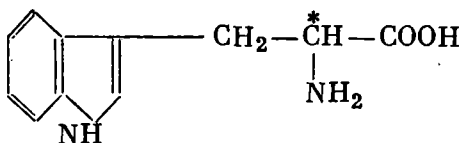
The reactions for the phenylhydrazones of acetophenone (the formation of α -phenylindole) and of propionaldehyde (the formation of β -methylindole) can be pictured similarly.

The heterocyclic half of the indole molecule is more reactive than the benzene half.

In chemical properties indole is in many respects like pyrrole: it darkens quickly upon exposure to air, mineral acids cause it to polymerize, and it imparts a red colour to a splint moistened with hydrochloric acid. The presence of the benzene ring, as usual, heightens acidic properties: indole scarcely exhibits any basic properties; on the contrary, the hydrogen atom of the NH group can be replaced by a metal, for example, by treatment with metallic potassium or even by fusing with caustic alkalis. The pyrrole resemblance of indole is also revealed by its reaction with pyridinesulphotrioxide: in this case the product at 100° is indole sulphonic-2 acid. Ordinarily, however, it is the β -hydrogen atom, with properties similar to the properties of an α -hydrogen atom of naphthalene, that enters into the reaction. For example, iodine in a weakly alkaline solution reacts with indole to produce 3-iodoindole. The organomagnesium derivatives of indole react with anhydrides to form ketones and with ethyl formate to give aldehydes. The ketone and aldehyde groups assume β -positions.

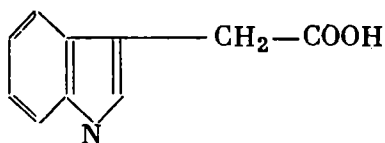
The indole derivatives are important biologically; some of them are utilized industrially.

307. Tryptophane. One of the important amino acids produced by the hydrolysis of proteins is α -amino- β -(indolyl-3)-propionic acid, or tryptophane (m.p. 289°):



The casein of milk, for instance, contains about 1.85% of L(—)-tryptophane. Animal organisms cannot synthesize tryptophane themselves; therefore their food should include proteins containing it.

308. Heteroauxin. Heteroauxin, or α -indolylacetic acid (m.p. 165°), belongs to the group of natural substances influencing the growth of plant cells and responsible for the phenomenon of phototropism:



heteroauxin

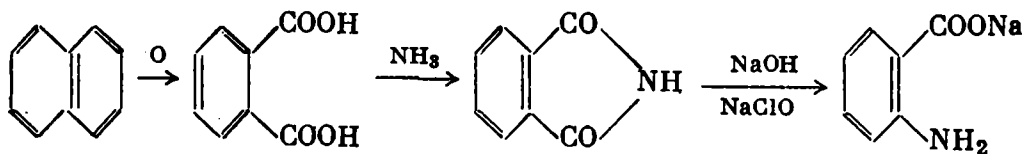
The first experiments that led to the discovery of these substances were performed by Darwin; but their chemical nature was not yet known then. Subsequently, these substances contained in plants were named *auxins*. Heteroauxin itself was first isolated by F. Kögl from human urine. Auxins were found in the tips of coleoptiles, the first leaves of gramineous plants to appear when the seeds germinate. Tiny amounts of auxins are contained in plants, which points to the tremendous potency of these substances. Kögl isolated 0.25 g of heteroauxin from urine. The isolation of such an amount of the substance from the seedlings, say, of maize would require the processing of about 2,000 million such seedlings. Pure heteroauxin was obtained by the Tsvet chromatographic technique (p. 542).

It should be pointed out that the name of growth substances sometimes applied to these compounds is not very fortunate, since it may suggest that the very property of plant growth is, so to say, inherent in them. This was, roughly, the theory expounded in the past century by the German physiologist J. Sachs. He assumed that the formation of plant organs, such as the stem, the roots, and the flowers, was due to special stem-, root-, and flower-forming substances. The fallacy of this theory was revealed by K. Timiryazev. The phytohormones described above are merely substances capable of stimulating or retarding natural processes in the plant organism. The mechanism

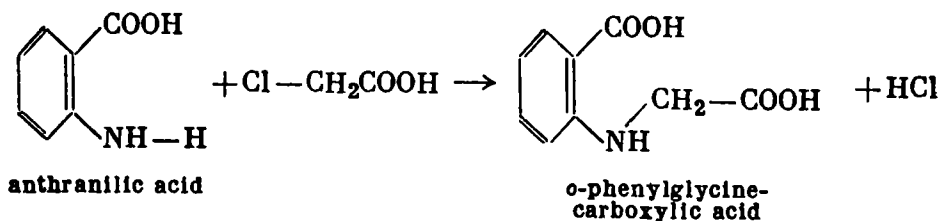
309. Indigo. Indigo was known in ancient Greece. The Greeks used to bring it from India, where it was obtained from plants of the *Indigofera* species. In Russia and elsewhere in Europe indigo was derived from the wood plant (*Isatis tinctoria*). The bright and fast colour imparted by indigo to fabrics made this a highly valuable dye.

The cardinal contribution to the study of indigo was, however, made by Baeyer; his work culminated in 1880 in the determination of the dye's structure and its synthesis.

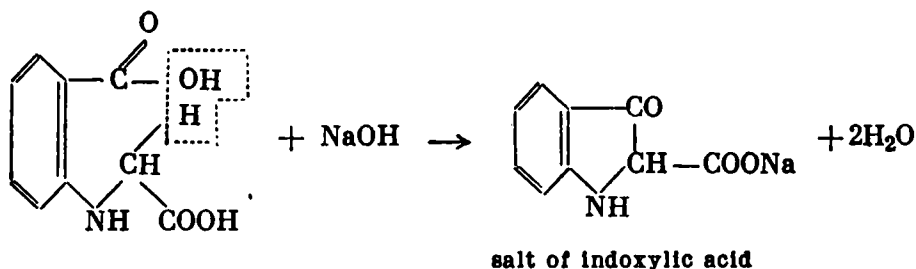
Baeyer's synthesis was highly complex and was not put to practical use. The first commercial synthetic indigo was prepared by the following procedure: naphthalene (from coal-tar) was oxidized to phthalic acid, which was converted to phthalimide and then, by means of the Hofmann reaction (p. 336), to anthranilic acid:



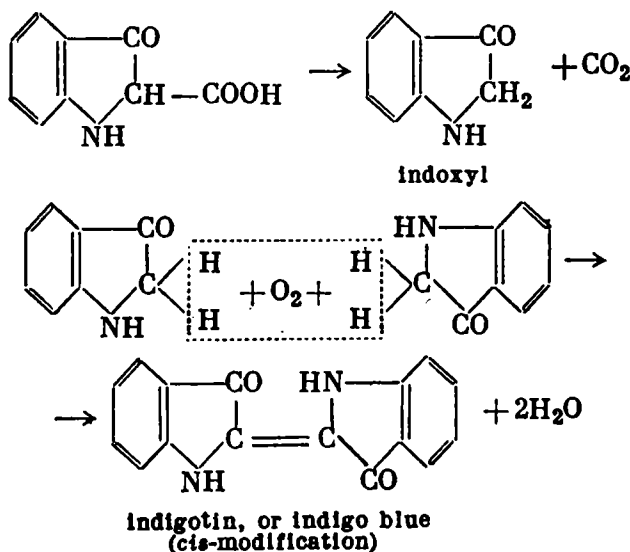
By treatment with chloroacetic acid, the anthranilic acid was converted to *o*-phenylglycinecarboxylic acid:



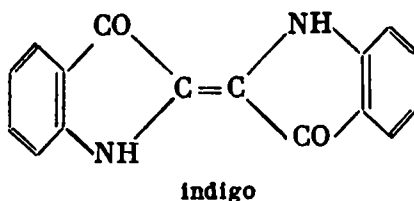
When the product is fused with an alkali, it loses water and the cycle is closed:



The passage of air through alkaline solutions of the indoxylate formed by fusion causes the loss of carbon dioxide, with the formation of an *indoxyl*; the latter is oxidized to indigo, which is precipitated in the form of blue flakes:

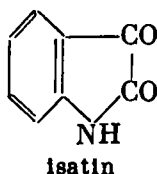


The latest findings indicate that indigo has a *trans*- rather than *cis*-structure:



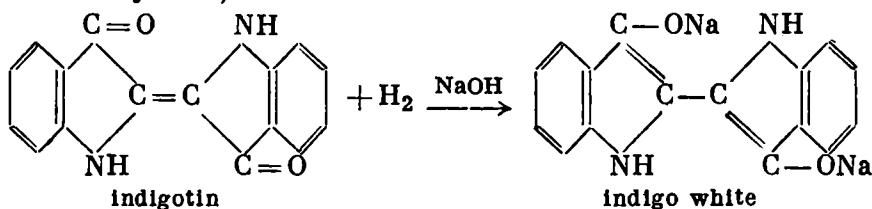
Indigotin, or indigo blue, is a blue powder. It melts at 390° and sublimes with partial decomposition. It does not dissolve in ordinary solvents, but does dissolve upon heating in aniline. Oxidation by nitric acid turns it into *isatin*, which forms orange-red crystals melt-

ing at 201°:



By distilling indigo with zinc dust, Baeyer obtained indole, whose structure he later confirmed by synthesis.

As indigo does not dissolve in water, its application to cloth is usually effected by transferring it into so-called *indigo white*, a leuco-compound. This is accomplished by carefully reducing indigo in an alkaline medium (which reduces the carbonyl groups that form a conjugated bond system):

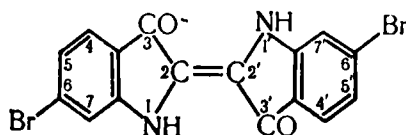


For dyeing the cloth is soaked in a colourless alkaline solution of indigo white and then exposed to the action of the air. Indigo white is very easily oxidized by the oxygen of the air and reconverted to the insoluble blue pigment. This is an example of the vat dyeing referred to earlier (p. 496).

The sulphonation of indigo blue with fuming sulphuric acid produces water-soluble indigo blue, or disulphoindigo acid, which is used for dyeing silk fabrics.

By brominating or chlorinating indigo, it is possible to obtain dyes with a greater immunity to friction and light.

In 1909-11 Friedländer investigated the "purple of the ancients" and established its structure. This dye was prepared in ancient times from Mediterranean sea-snails by a very complicated and expensive procedure. Friedländer's entire investigation was carried out with 1.4 g of purple, which had been extracted from 12,000 sea-snails. It was found that the "purple of the ancients" was dibromoindigo, with the halogen atoms in positions 6 and 6':



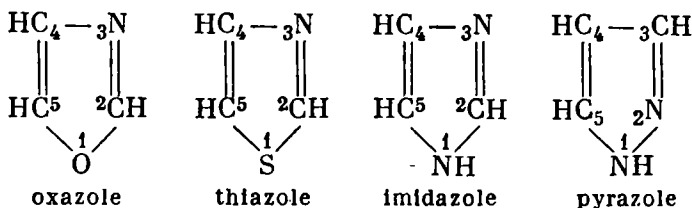
"Purple of the ancients"

When indigo is brominated, the halogen atoms go to positions 5,5' and 7,7', forming a blue dye.

AZOLE GROUP

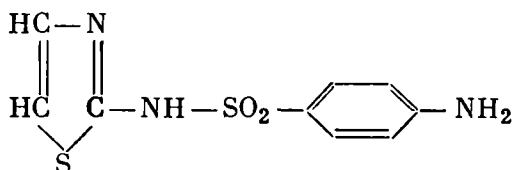
The azoles are five-membered heterocyclic compounds containing two hetero-atoms of which at least one is nitrogen.

The principal azoles are:



The representatives of these groups are numerous and diverse. We shall consider only a few of them.

310. Sulphathiazole. Sulphathiazole (m.p. 202°) is a drug related in structure to prontosil (p. 470):



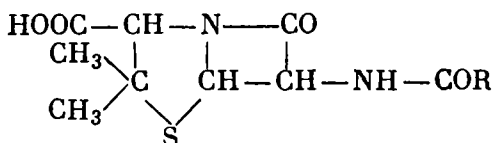
It is prepared in the same way as prontosil, but 2-aminothiazole is used instead of ammonia.

311. Penicillin. In 1928 Dr. Alexander Fleming, the British microbiologist, observed how a mould introduced by chance into a laboratory specimen halted the growth of a staphylococcal colony. Fleming attributed this action to a substance produced by the mould; he named the substance *penicillin*. It is now one of the most important antibiotics, i.e., substances which are developed by various organisms and which are capable in small doses of inhibiting the activity of microbes.* Penicillin is produced by certain varieties of the mould *Penicillium*. During the Second World War a group of British biologists and chemists isolated and investigated the bactericidal substances produced by the mould. It was found that penicillin is capable of inhibiting putrefactive bacteria even when it is diluted in water 1 : 50,000,000 parts. Yet higher concentrations of penicillin have no toxic effect on human beings.

Chemical analysis revealed that penicillin is a mixture of substances of similar structure. Its general formula incorporates the

* The antibiotic action of moulds was first established in 1870-71 by the Russian physicians V. Manassein and N. Polotebnev, who in the course of several investigations demonstrated that moulds could be used to cure purulent ulcers, furunculosis, etc.

heterocyclic system of thiazolidine, i.e., hydrogenated thiazole:



In different types of penicillin the radical R is different:

Penicillin F contains the radical $-\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2\text{CH}_3$ (pentenyl)

Penicillin G contains the radical $-\text{CH}_2\text{C}_6\text{H}_5$ (benzyl)

Penicillin X contains the radical $-\text{CH}_2\text{C}_6\text{H}_4\text{OH}$ (hydroxybenzyl)

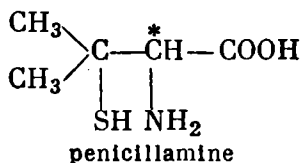
Penicillin K contains the radical $-\text{CH}_2(\text{CH}_2)_5\text{CH}_3$ (*n*-heptyl)

Penicillin V contains the radical $-\text{CH}_2\text{OC}_6\text{H}_5$ (phenoxyethyl)

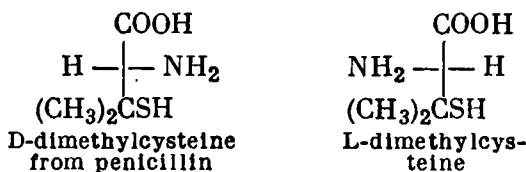
In 1957 Shiha and co-workers in the United States carried out the full synthesis of phenoxyethylpenicillin.

The structural formula of penicillin suggests a low chemical stability, due to the four-membered lactam cycle. Indeed, when treated with acids, penicillin hydrolyzes readily.

One of the products of the hydrolysis of penicillin is α -amino- β -thioacid (dimethylcysteine), which has been named *penicillamine*:



This acid has been found to belong to the series of dextrorotatory amino acids rather than to the laevorotatory series to which all the amino acids of the common natural proteins belong:

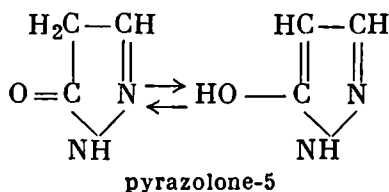


In the U.S.S.R. penicillin and other antibiotics are produced on a large scale.

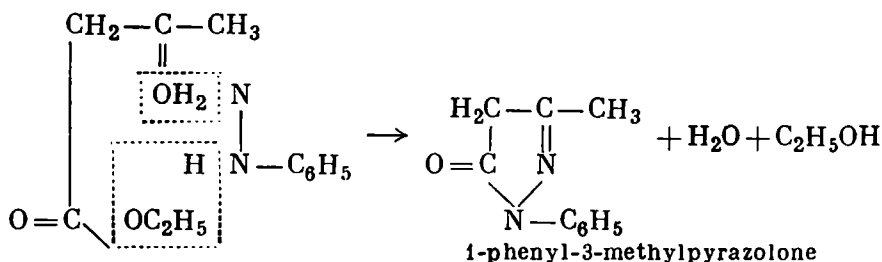
A big contribution to the study of penicillin and its production in the U.S.S.R. has been made by Professor Z. Yermolyeva.

A highly important antibiotic, which is used in the treatment of several diseases, is one that is produced by a microbe of the soil. The molecule of this antibiotic, discovered in 1942 by G. Gauze and M. Brazhnikova and called *gramicidin S* (Soviet), contains a complex cyclic decapeptide of five pairs of amino acids (namely proline-, valine-, ornithine-, leucine-, and phenylalanine) in equimolecular amounts. The first four amino acids have L-configurations, while phenylalanine belongs to the D-series. The full synthesis of this antibiotic was accomplished in Switzerland in 1956 (R. Schwitser and P. Sieber).

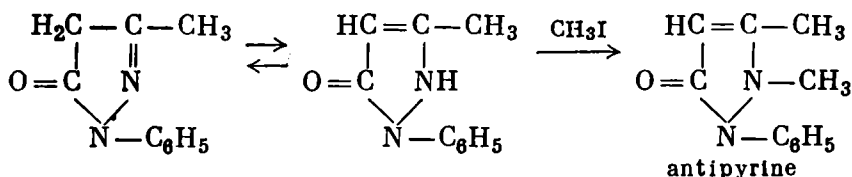
312. Antipyrine and Pyramidon. The substituted pyrazolone group includes several drugs:



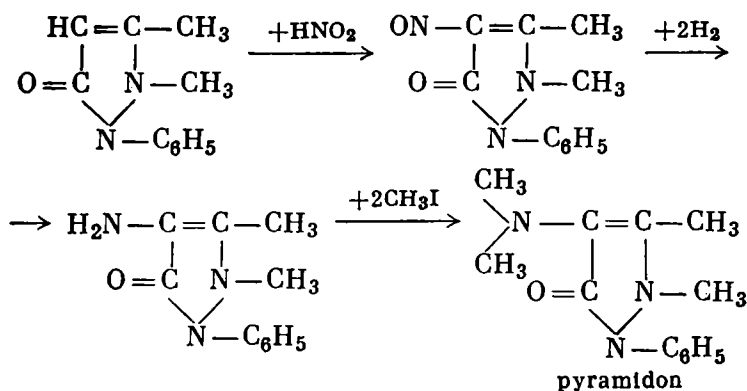
When phenylhydrazine is heated with ethyl acetoacetate, the product is 1-phenyl-3-methylpyrazolone:



One of its derivatives is *antipyrine*, which is used as an antipyretic. It is prepared by treating phenylmethylpyrazolone with methyl iodide or methyl sulphate. The phenylmethylpyrazolone reacts in tautomeric form:

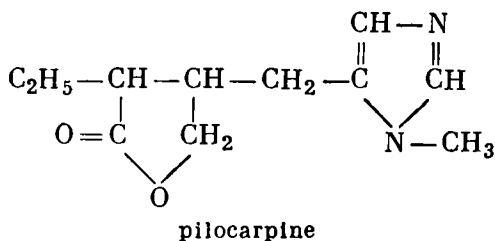


Dimethylaminoantipyrine is known as *pyramidon* and is used as an antipyretic and antineuralgic drug. It is prepared as follows. Antipyrine is treated with nitrous acid; a nitroso group is introduced into position 4 and is then reduced to an amino group; the product is treated with methyl iodide:



There is an interesting history to the discovery of the medicinal value of antipyrine and its derivatives. In the eighties of the past century L. Knorr, when studying one of the condensation products of ethyl acetoacetate and phenylhydrazine, mistook it for a derivative of hydrogenated quinoline. In the belief that the substance had the properties of quinine, he decided to test it as a drug; to improve its solubility he treated it with methyl iodide. Tests revealed the drug's antipyretic effect, after which it was introduced into medical practice as "antipyrine". The discovery focussed great interest on the medical potentialities of the pyrazolone derivatives.

313. Pilocarpine. The imidazole group includes the highly valuable alkaloid pilocarpine (m.p. 34°), obtained from certain types of African plants:

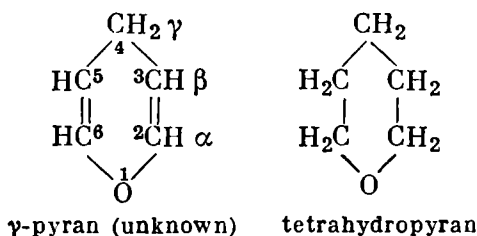


Pilocarpine stimulates the activity of the salivary, sudoriferous, and digestive glands. It is especially important in the treatment of eye diseases because it causes a contraction of the pupils and diminishes intraocular tension. Pilocarpine was first synthesized in 1936 by N. Preobrazhensky.

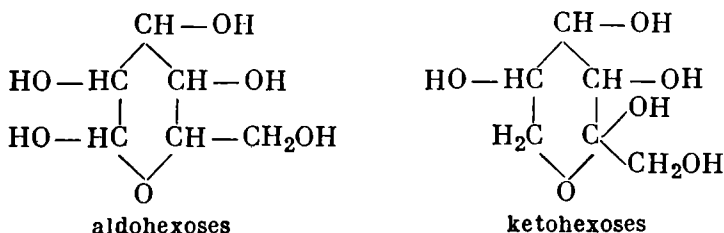
Six-Membered Heterocyclic Compounds

PYRAN GROUP

The most important of the six-membered heterocyclic compounds containing one oxygen atom are the derivatives of γ -pyran (1,4-pyran). Gamma-pyran itself has not been obtained so far. Its tetrahydro-derivative is an inner ether of pentandiol-1,5, from which it can be obtained by heating with 60% sulphuric acid:

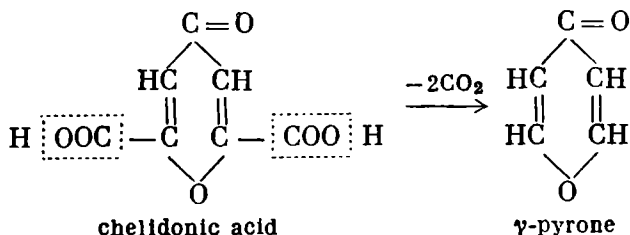


It should be remembered that the hexoses — both aldoses and ketoses — are cyclic systems, mostly six-membered heterocyclic pyranoses:

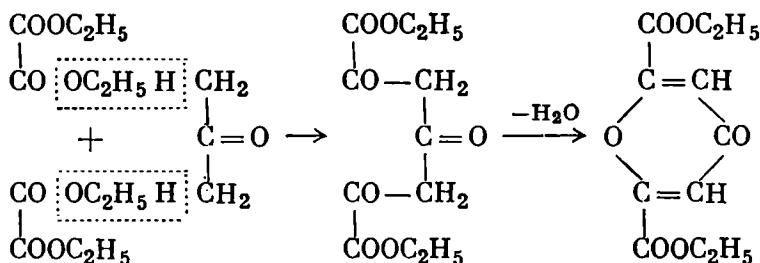


Derivatives of oxidized pyran, or γ -pyrone, occur extensively in nature. But before turning to them, mention should be made of the peculiar properties of the simplest derivatives of γ -pyrone.

314. Gamma-Pyrone and Pyroxonium Salts. Gamma-pyrone (m.p. 32.0°; b.p. 217°) was first prepared by decarboxylizing *chellidonic acid*:



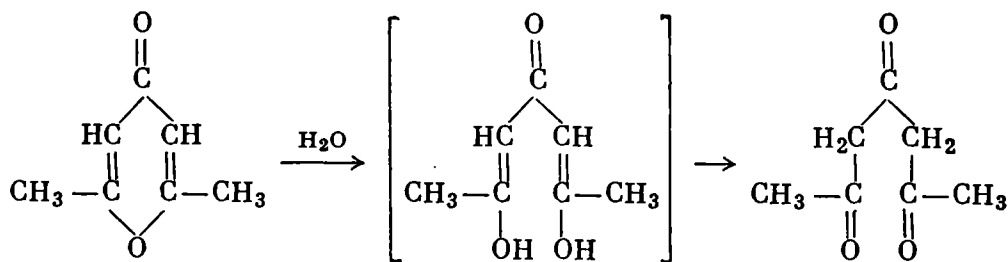
Chelidonic acid (γ -pyrone-2,6-dicarboxylic acid) owes its name to the fact that it was first derived from the plant celandine, or *Chelidonium majus*. It was synthesized from ethyl oxalate and acetone:



The first stage of the reaction is a Claisen condensation under the action of sodium ethylate; ring closure is effected by boiling the product with hydrochloric acid.

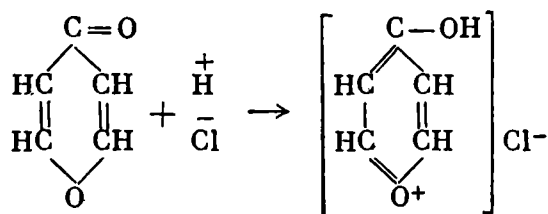
Gamma-pyrone dissolves readily in water; the solution is neutral. The properties of γ -pyrone and its derivatives are somewhat peculiar. For one thing, the presence of the carbonyl cannot be established by the usual reagents: hydroxylamine or phenylhydrazine. Furthermore, reduction proceeds with difficulty. The hydrogenation of γ -pyrone with hydrogen in the presence of palladium produces tetrahydropyrone. Gamma-pyrone exhibits certain aromatic properties: treatment with bromine in the presence of ferric chloride yields a yellow addition product, a perbromide, which is converted by steam distillation to 3-bromo- and 3,5-dibromopyrone.

The γ -pyrone ring is sensitive to alkalis, and the oxygen link is easily ruptured. The treatment of 2,6-dimethylpyrone with an alkali, for example, yields a triketone, heptanetrione:

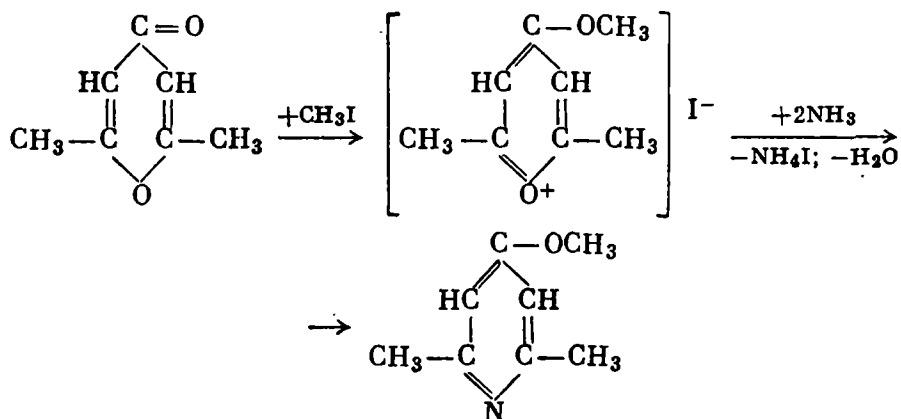


The most peculiar property of the γ -pyrones is their ability to react with strong acids, forming salts of the oxonium type (so-called *pyroxonium salts*). The oxonium salts are formed by the addition of a hydrogen ion to various oxygen-containing compounds (at the expense of the free electron pair of the oxygen atom), the reaction proceeding similarly to the formation of ammonium salts.

Pyroxonium salts are formed as follows:

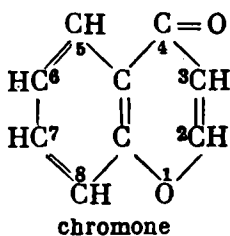


The addition of a proton gives the pyrone nucleus a structure similar to that of benzene, while the oxygen atom acquires a positive charge. That this is what happens is confirmed by the addition of alkyl iodides to pyrone and its derivatives. For instance, 2,6-dimethylpyrone reacts with methyl iodide to form 4-methoxy-2,6-dimethylpyroxonium iodide, which is converted by the action of ammonia to the more familiar 4-methoxy-2,6-dimethylpyridine:



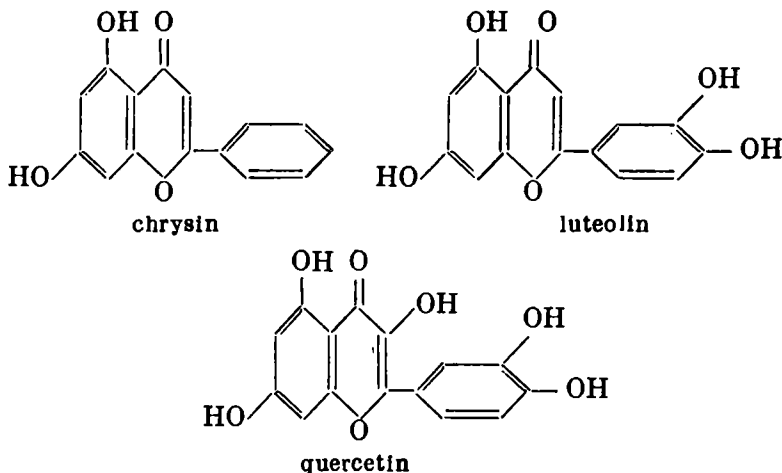
When salts are formed, γ -pyrone is thus converted to a compound similar to benzene, which may apparently be the reason for the stability of γ -pyrone under acid treatment.

315. Chromone. Many natural pigments are known that are derivatives of benzopyrone, or chromone (m.p. 59°):



Many yellow and brown pigments from the bark and wood of plants, as well as from flowers, are hydroxy derivatives of 2-phenylchromone, or *flavone* (from the Latin *flavus* meaning yellow). Flavone is contained in the pollen covering the surface of some flowers and leaves.

Chrysin (dihydroxy flavone) is a yellow pigment that occurs in poplar buds. **Luteolin** (tetrahydroxy flavone) has been isolated from the petals of the yellow mignonette and certain other flowers. **Quercetin** (pentahydroxy flavone) is a pigment occurring in the American dyer's oak (*Quercus tinctoria*). The bark of this oak serves to dye silk and wool. Quercetin has also been found in many other plants, such as hop, tea, yellow stock, and coltsfoot.



Most of the flavones are yellow solids with high melting points, which are soluble in alcohol, aqueous solutions of alkalis (phenolic properties), and acids (oxonium character). With ferric chloride they give characteristic colours: dark green and reddish brown.

316. Anthocyanins. The bright colours of many flowers and fruits are due to the presence of many pigments, often closely related in structure and chemical character. These pigments were first separated by the Tsvet chromatographic technique (p. 542).

Willstätter*, the pioneer investigator of these substances, named them anthocyanins.** It is noteworthy that the diverse colours of flowers are produced by compounds of very similar structure.

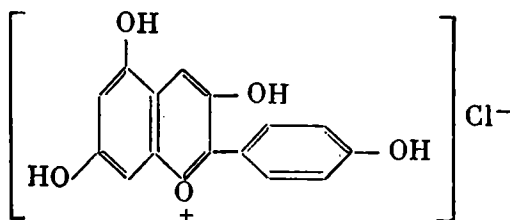
The anthocyanins are glucosides, i.e., substances containing carbohydrates and compounds of non-carbohydrate structure, or anthocyanidins. The yellow pigments, as stated above, are derivatives of the phenylchromone (flavone) group.

* Richard Willstätter (1872-1942) was an outstanding German organic chemist. His most important work was in the study of the structure of chlorophyll, in the chemistry of ferments, and the assimilation of carbon dioxide by plants. For his scientific achievements Willstätter was elected a foreign member of the Academy of Sciences of the U.S.S.R.

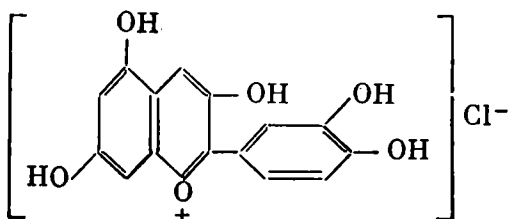
** From the Greek *anthos* meaning flower.

The pigments of red and blue flowers belong to the group of salts of less oxidized chromone.

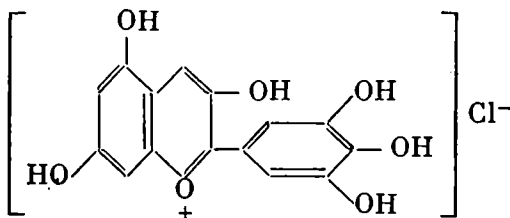
The pigments encountered most frequently as salts are *pelargonidin*, *cyanidin*, and *delphinidin*:



pelargonidin chloride



cyanidin chloride

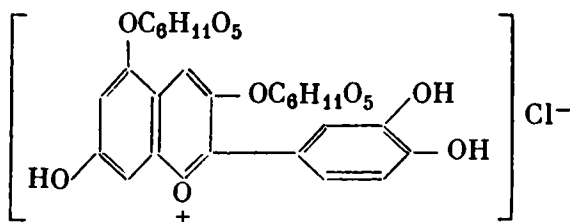


delphinidin chloride

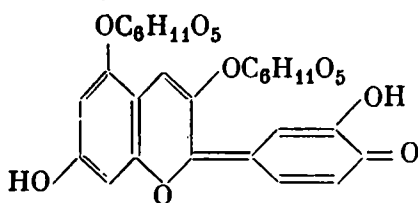
The similarity of these anthocyanidins and their distinctions become apparent when they are fused with alkalis. This causes the breakdown of the pyran ring. The left part of the molecule, similar in all the compounds, is converted to phloroglucinol (1,3,5-trihydroxybenzene). The right parts of the molecules yield: pelargonidin, *p*-hydroxybenzoic acid; cyanidin, protocatechuic acid; delphinidin, gallic (3,4,5-trihydroxybenzoic) acid. The structure of the anthocyanins was confirmed by their synthesis.

The anthocyanins are coloured substances. Their colour depends upon several factors. The more oxygen atoms there are in the molecule, for example, the bluer the pigment. The acid salts of the anthocyanins are usually red; the combination of metal salts with anthocyanin bases produces blue hues. In the neutral state the pigments are violet. For instance, the pigments of the cornflower and the red rose are both red at $\text{pH} = 3.0$ and less, whereas at $\text{pH} = 11.0$ both are blue. The drastic change in colour appears to be due to a change

in the structure of cyanidin:



cyanidin oxonium salt



cyanidin base

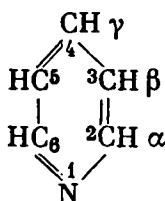
When fruit is kept in tins, there is often a change of colour owing to the formation of compounds of the pigment with tin salts.

The content of the pigment in petals varies within a wide range. For instance, the content of the pigment in the cornflower (in dry weight) is only 0.75%; in red dahlias, up to 20%, and in dark blue pansies, up to 33%.

PYRIDINE GROUP

317. Pyridine. Pyridine, its homologues, and other pyridine bases were first discovered in the oil produced by the dry distillation of bones. Nowadays the material for making pyridine is coal-tar.

Pyridine is a colourless liquid with a characteristic disagreeable odour (m.p. -42° ; b.p. 115° ; $d_4^{20} = 0.982$):

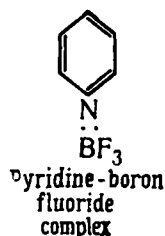
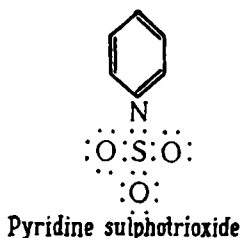
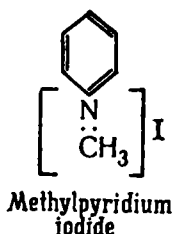
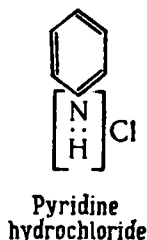


pyridine

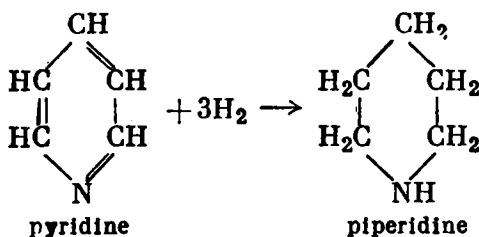
Pyridine is miscible with water in all proportions. It is a very good solvent for many organic compounds, as well as for many inorganic salts (CuCl_2 , Cu_2Cl_2 , ZnCl_2 , HgCl_2 , AgNO_3). A solution of potassium permanganate in pyridine is often used for oxidizing organic substances. In some of its properties pyridine resembles benzene. Like benzene, it is highly stable to the action of acids and oxidizing agents.

Pyridine is a tertiary amine and has noticeable, but not very pronounced basic properties: it forms salts with acids and yields many addition products with acid anhydrides and with various salts and halogenides.

The addition is effected by the free electron pair of the nitrogen:

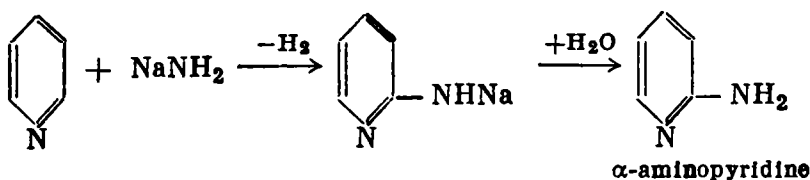


Nascent hydrogen (produced, for example, by the action of metallic sodium in an alcoholic medium), as well as hydrogen in the presence of platinum, reduces pyridine to hexahydropyridine, or *piperidine*:

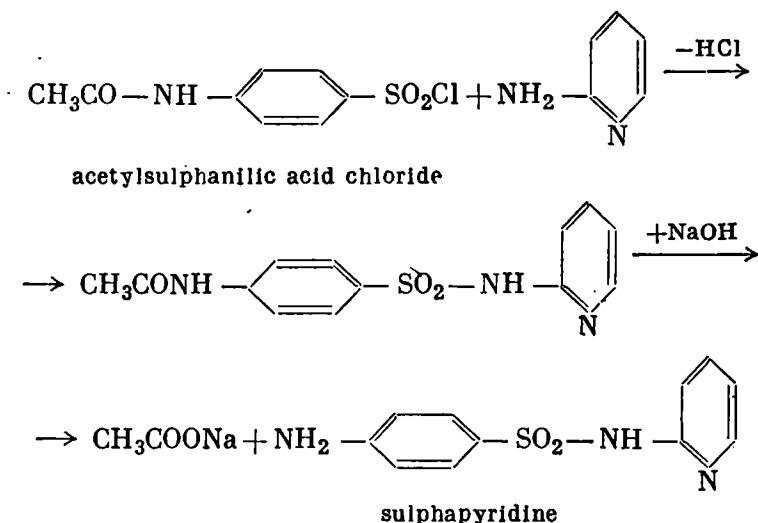


The action of chlorine or bromine on pyridine at first yields unstable products of the addition of the halogen to nitrogen. The halogen can be introduced into the ring (into β -position) only at 300-400°. Similarly, only when pyridine is heated with concentrated sulphuric acid above 300°, is it possible to obtain pyridinesulphonic-3 acid. 3-Nitropyridine is prepared by nitrating pyridine with a mixture of saltpetre and sulphuric acid at 300°.

Reactions with alkaline reagents proceed much more readily. When pyridine is heated with sodium amide, α - and γ -aminopyridines form readily (A. Chichibabin):

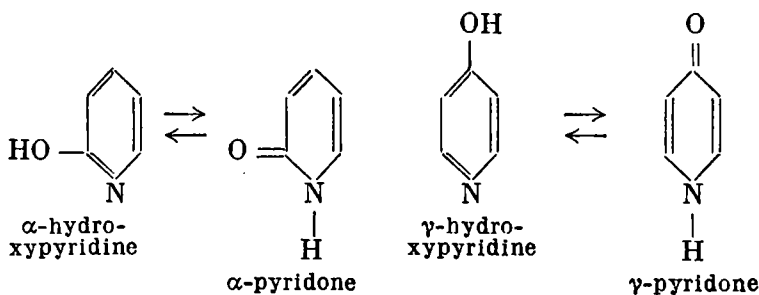


Alpha-aminopyridine (m.p. 57.5°) is used to prepare many pyridine derivatives. It serves to prepare the very important sulpha drug

sulphapyridine:

Sulphapyridine is used in the treatment of very many infectious diseases (especially, membranous pneumonia and meningitis).

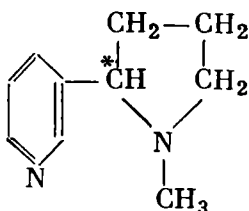
Caustic alkalis, upon heating, have the same effect on pyridine as sodium amide has: hydrogen is released and 2- and 4-hydroxypyridines are formed. The same compounds can be prepared by the action of nitrous acid upon corresponding aminopyridines. The hydroxypyridines are like phenols: they give a colour reaction with ferric chloride and dissolve in aqueous alkalis. The α - and γ -hydroxypyridines are solids (the m.p. of α -hydroxypyridine is 107° ; γ -hydroxypyridine melts at 148°); they undergo tautomeric transformations to keto compounds called *pyridones*:



Carboxylic acids of pyridine can be prepared by treating pyridine homologues and other derivatives with strong oxidizing agents. For example, 2-methylpyridine (α -picoline) yields picolinic acid. Mention should be made of *nicotinic* (pyridine-carboxylic-3) *acid* (m.p. 234°), which can be prepared by oxidizing nicotine by nitric acid or by heating quinolinic acid (p. 565). The acid is one of the most

important constituents of the mixture of substances that make up vitamin B. Nicotinic acid is usually called vitamin PP. A lack of this vitamin gives rise to the severe illness known as pellagra.

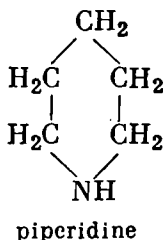
318. Nicotine. The derivatives of pyridine include the very important alkaloid *nicotine* $C_{10}H_{14}N_2$:



The leaves of tobacco (*Nicotiana tabacum*) and shag contain up to 2-3% of nicotine (b.p. 247°) in the form of its citrate. Tobacco was first brought to Europe from America in 1550 by the French Ambassador to Portugal Jean Nicot; the names of the plant and the alkaloid are derived from his name. The natural alkaloid is laevorotatory. Nicotine was first synthesized by Pictet in 1904.

Nicotine is one of the strongest poisons, nearly as potent as prussic acid. It is noteworthy that laevorotatory (natural) nicotine is more than twice as toxic as the dextrorotatory isomer. A cheap source of nicotine are the shag and the tobacco dust that are waste materials at tobacco factories. Aqueous extracts containing nicotine are used as most potent insecticides.

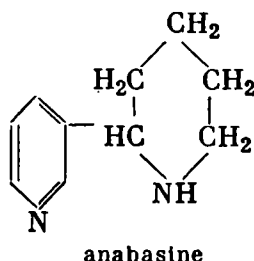
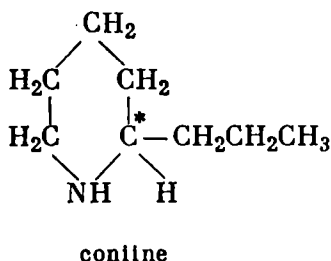
319. Piperidine. The reduction of pyridine by sodium in an alcoholic solution (Vyshnegradsky reaction) yields hexahydropyridine, or piperidine (m.p. -9° ; b.p. 106°). It is a strong secondary amine



The piperidine ring is a constituent of many alkaloids (A. Vyshnegradsky), of which one of the simplest in composition is the alkaloid of the poisonous plant hemlock *Conium maculatum*. This alkaloid, called *coniine* (b.p. 166°), is α -propylpiperidine. The coniine formula contains one asymmetric carbon atom. The natural alkaloid is dextrorotatory.

In 1930 A. Orekhov isolated and investigated the alkaloid contained in the weed *Anabasis aphylla*, which is widespread in Central

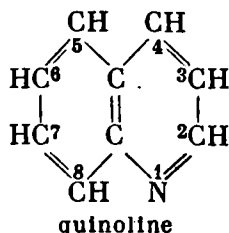
Asia. He named this alkaloid *anabasine*



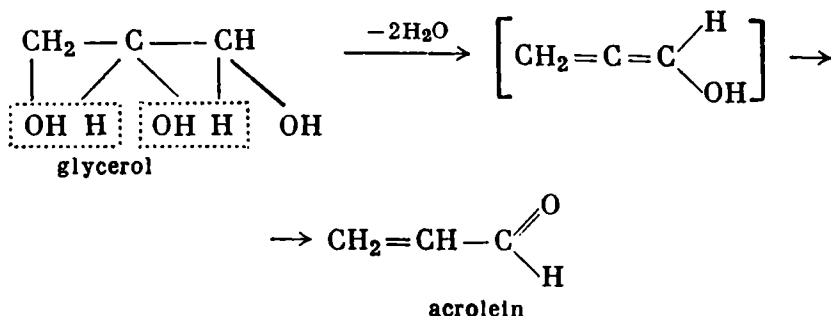
Anabasine is a liquid boiling at 145° at a pressure of 15 mm Hg. In chemical composition it is α -(β -pyridyl)-piperidine. Anabasine is thus an isomer of nicotine, in whose formula methylpyrrolidine has been replaced by piperidine. Anabasine is a potent insecticide. It is used either as a free base or, more often, as a salt, anabasinesulphate.

QUINOLINE GROUP

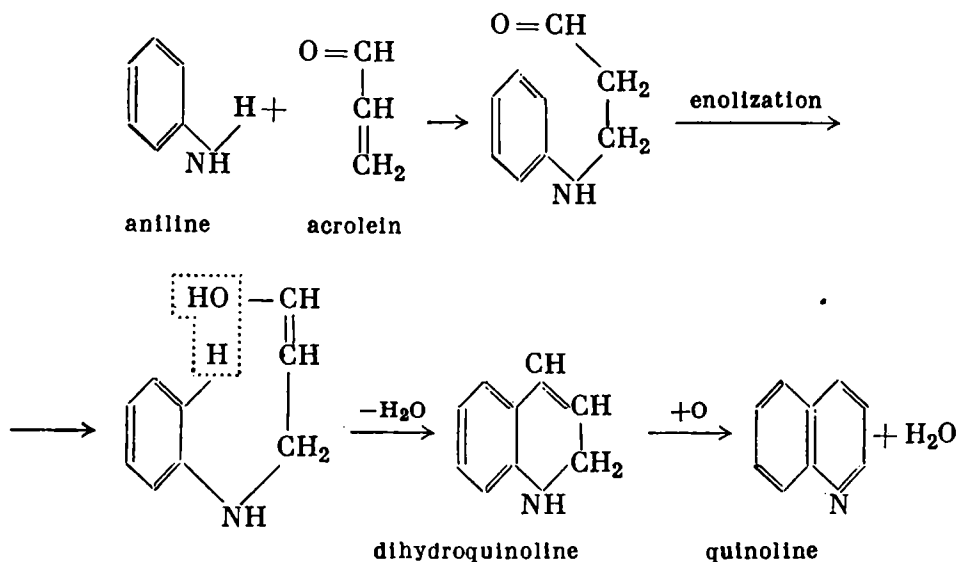
320. Quinoline. Quinoline C_9H_7N is benzopyridine. In structure and several of its properties it is like naphthalene



Quinoline was first obtained in 1842 by Gerhardt, who distilled a mixture of the alkaloids of cinchona bark with sodium hydroxide. The structure of quinoline is established by several syntheses, as well as by its reactions. Quinoline is usually prepared by the Skraup synthesis, which consists in heating a mixture of aniline, glycerol, and nitrobenzene in sulphuric acid. There are evidently several stages to the synthesis. The sulphuric acid causes the glycerol to give up water and turn into *acrolein*:

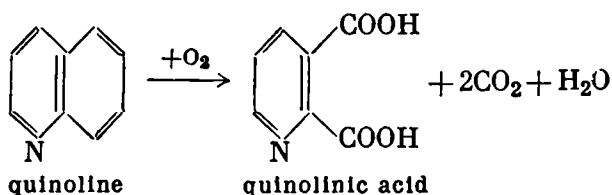


The acrolein reacts with aniline to form an addition product, which under the influence of the sulphuric acid condenses to dihydroquinoline. The latter is oxidized by nitrobenzene to quinoline:



Quinoline and its homologues are contained in coal-tar. Quinoline is a high-boiling liquid (m.p. -19.5° ; b.p. 237.7°); it has a low solubility in water. Another of its features is a characteristic odour.

The chemical properties of quinoline become clear at once if we regard it as benzopyridine. Like pyridine, it is a weak tertiary base: with mineral acids it forms salts, while with alkyl iodides it yields quaternary ammonium salts. Upon oxidation, say, by potassium permanganate, the pyridine half of the molecule, as the more stable, does not change; the product is pyridine-carboxylic-2,3 acid, or *quinolinic acid*:

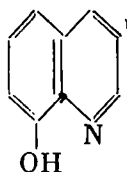


Like pyridine, quinoline, when treated with sodium amide, yields α - and γ -aminoquinolines (Chichibabin reaction). When quinoline is fused with potassium hydroxide, the product is α -hydroxyquinoline, which, like hydroxypyridine, is capable of undergoing a transformation into the keto modification, *carbostyrl*.

Oxygen-containing reagents attack the pyridine ring with great difficulty, and substitution therefore ordinarily takes place in the benzene ring of quinoline. Certain regularities govern this, just as in the case of naphthalene: the most reactive positions in the quinoline molecule, corresponding to the α -positions in naphthalene, are the 5 and 8 positions. When, for instance, quinoline is nitrated, the immediate products are mononitroquinolines, a mixture of roughly equal quantities of 5-nitroquinoline and 8-nitroquinoline. Quinoline was first sulphonated by N. Lyubavin in 1870. Fuming sulphuric acid in the cold produces 8-sulphoquinoline, which upon heating undergoes a rearrangement to 6-sulphoquinoline in the same manner that α -naphthalenesulphonic acid is converted to its γ -isomer.

The reduction of quinoline was first accomplished by A. Vyshnegradsky. Upon hydrogenation, the hydrogen first enters the pyridine half of the molecule; dihydro- and tetrahydroquinoline are formed.

Another quinoline derivative that should be mentioned is 8-hydroxyquinoline:



8-hydroxyquinoline

It can be prepared by the action of a caustic alkali on a corresponding sulpho-derivative. Another name for 8-hydroxyquinoline is *oxine*.

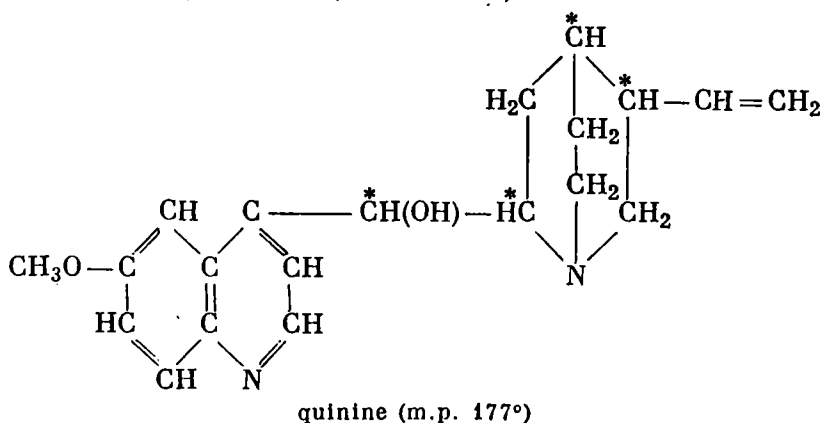
This has proved a very valuable analytical reagent. By means of oxine it is possible to detect and quantitatively estimate copper, zinc, cadmium, and other metals in the form of insoluble precipitates (complexes).

321. Quinine and Other Antidotes to Malaria. Quinine is a very important drug, used in the treatment of malaria. It belongs to the alkaloid group. His study of quinine and other vegetable bases prompted A. Vyshnegradsky to suggest in 1878-80 that many plant alkaloids were derivatives of pyridine and quinoline. Subsequent investigations of many alkaloids confirmed this.

Quinine, as well as many other, structurally related alkaloids, is contained in the bark of the cinchona tree, whose medicinal value became known in Europe as far back as the 17th century.

The investigations of the structure and properties of quinine carried out by several scientists were of great practical importance. Quinine was isolated from the mixture of alkaloids contained in cinchona bark and its chemical structure was established.

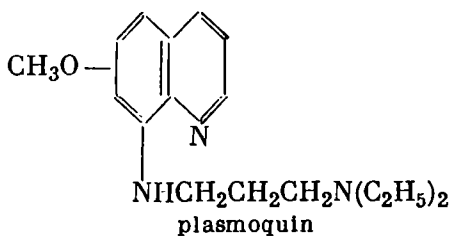
The formula of quinine is now quite clear and has been corroborated by its full synthesis (Woodward):



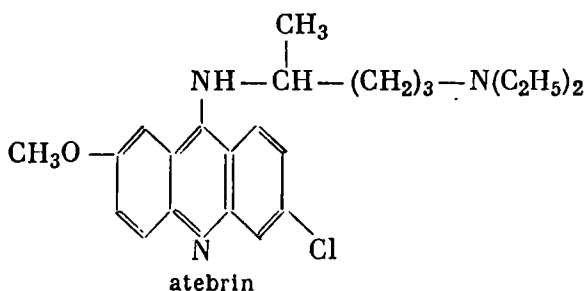
It is clear from this formula that the quinine molecule contains two tertiary nitrogen atoms; quinine can form salts with mineral acids. The quinine molecule has four asymmetric carbon atoms. An alcoholic solution of natural quinine is strongly laevorotatory: $[\alpha]_D = -144^\circ$.

Although quinine has been synthesized in the laboratory, there is little prospect at present of synthetic quinine being manufactured industrially.

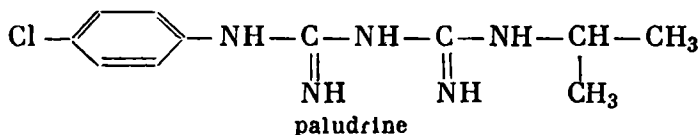
The study of the many synthetic compounds similar to quinine in chemical structure led to the discovery of a large number of drugs with an action like that of quinine. These include several derivatives of quinoline, among them *plasmoquin*, which was obtained practically at the same time in the U.S.S.R., in Germany, and in France:



Another widely used anti-malarial is *atebrin*:

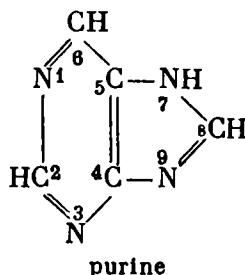
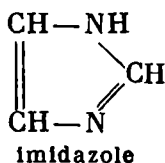
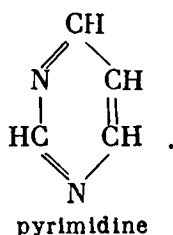


Atebrin is a derivative not of quinoline (benzopyridine), but of acridine (dibenzopyridine); structurally it has certain points of similarity with quinine and with drugs of the plasmoquin type. No simple relationship can, however, be established between chemical structure and medicinal properties. One anti-malarial that has no structural similarity with quinine is *paludrine*:



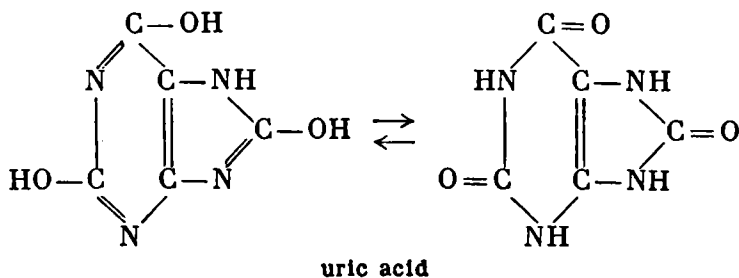
PURINE GROUP

The parent substance of this group is purine (m.p. 216°). In its molecule the pyrimidine ring is condensed with the imidazole ring:

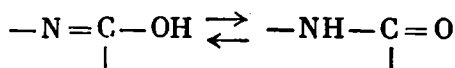


Purine has not been found as a natural product, but many substances whose molecules contain the purine ring are widespread in the organic world and are very important physiologically.

322. Uric Acid. The formula of uric acid, $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$, can be derived from the formula of purine by substituting hydroxyls for three hydrogen atoms. Uric acid is 2,6,8-trihydroxypurine, but it exists in tautomeric forms:



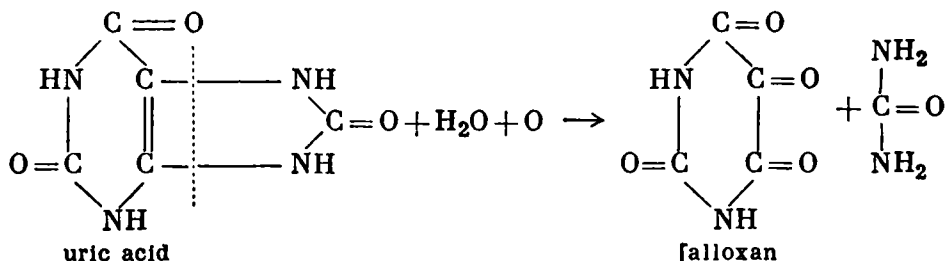
The tautomeric transformation involves the rearrangement:



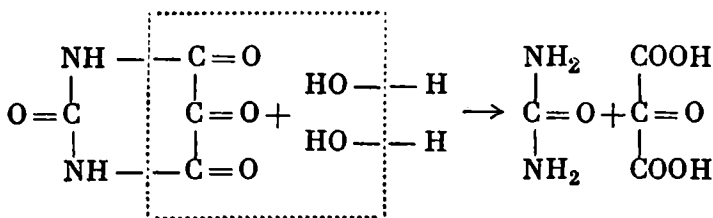
In the uric acid molecule two urea residues are linked by a chain of three carbon atoms.

Uric acid and urea are the principal products of nitrogenous metabolism in the animal organism. Small quantities of uric acid are contained in the human urine. It is the chief constituent of the excrement of birds and reptiles; in fact, it accounts for 90% of the excrement of the boa constrictor. When a person suffers from gout, uric acid is deposited in his joints; urinary calculi also consist primarily of this acid. Uric acid for industrial purposes is usually produced from guano, the accumulation of bird excrement found on islands of South America. The acid is a colourless crystalline powder with a very low solubility in water. It has faint acidic properties; two of the hydrogen atoms in its molecule can be replaced by a metal. When nitric acid is added to uric acid and the mixture is evaporated, a yellowish brown residue is formed; after the addition of a small amount of ammonia, the residue gives a beautiful purple coloration. This so-called murexide test serves for the qualitative detection of uric acid. The colour is due to the formation of *murexide* $C_8H_8N_6O_6$, the ammonium salt of *purpuric acid* $C_8H_5N_5O_6$.

The oxidation of uric acid by nitric acid produces *alloxan* and urea:



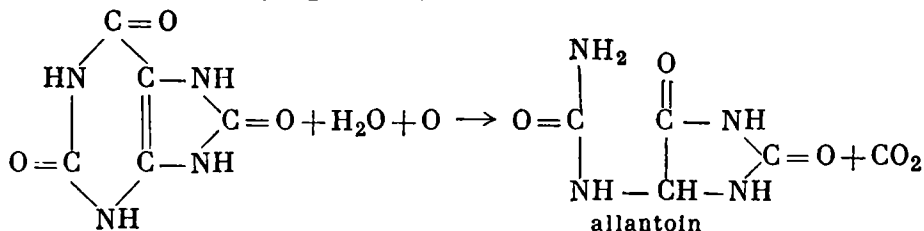
The structure of alloxan is confirmed by the fact that treatment with alkalis decomposes it to urea and *mesoxalic acid**:



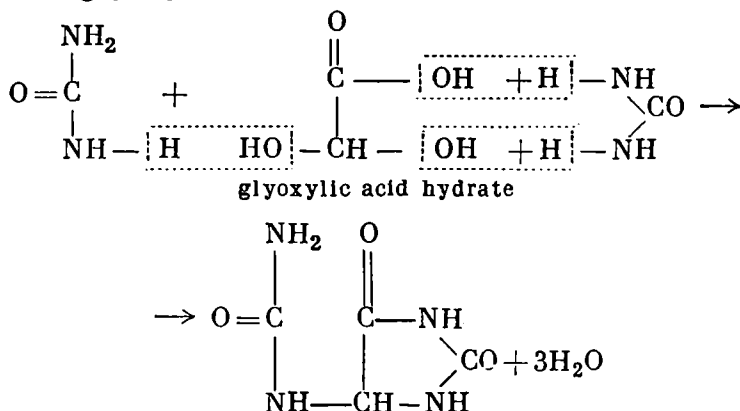
The fact that the oxidation of uric acid produces alloxan is an indication that the uric acid molecule contains a pyrimidine ring.

* Mesoxalic acid can be prepared by treating dibromomalonic acid $\text{HOOC}-\text{CBr}_2-\text{COOH}$ with an alkali.

When uric acid is oxidized with potassium permanganate, the product is *allantoin* (m.p. 238°):

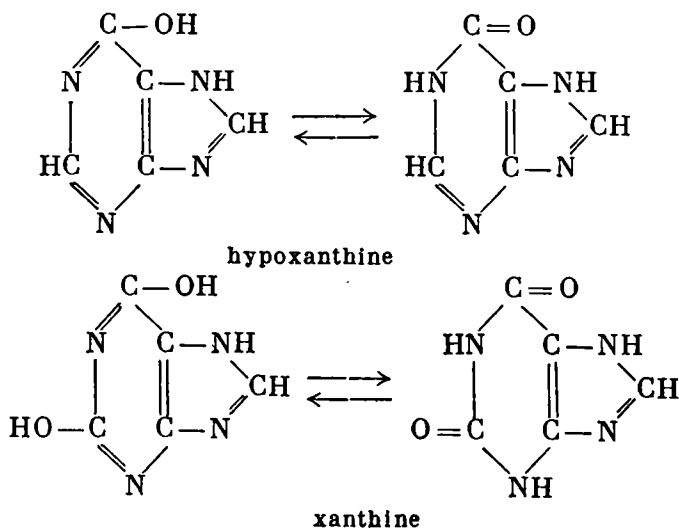


The structure of allantoin is confirmed by the fact that it can be prepared from glyoxylic acid and urea:



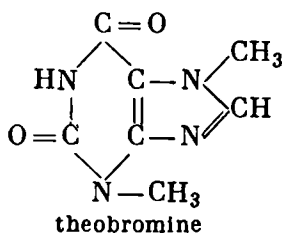
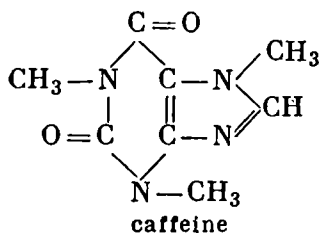
The formation of allantoin as a result of uric acid oxidation proves that the uric acid molecule contains the imidazolone ring.

323. Some Other Substances of the Purine Group. *Hypoxanthine* $\text{C}_5\text{H}_4\text{N}_4\text{O}$ and *xanthine* $\text{C}_5\text{H}_4\text{N}_4\text{O}_2$, like uric acid, can be regarded as hydroxy derivatives of purine. Hypoxanthine is 6-hydroxypurine, while xanthine is 2,6-dihydroxypurine. Both compounds exist in tautomeric forms:



Xanthine is found in many animal tissues, in the blood, in urine, in the liver, and in urinary calculi. It is a crystalline substance with a poor solubility in water; it forms salts with acids and bases. Hypoxanthine possesses amphoteric properties; in animal organisms it usually occurs with xanthine.

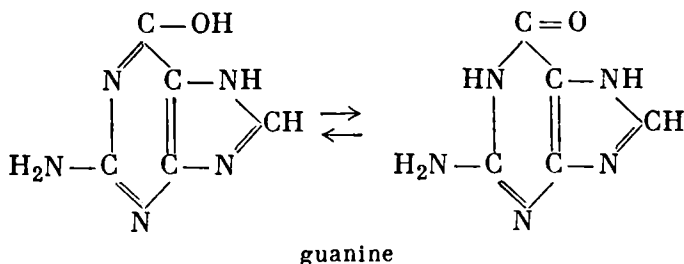
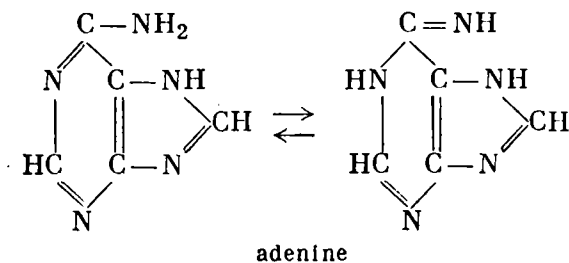
Caffeine $C_8H_{10}N_4O_2$ and *theobromine* $C_7H_8N_4O_2$ are methyl derivatives of xanthine:



Caffeine (1,3,7-trimethylxanthine) occurs in the leaves and beans of the coffee plant and in tea leaves. It crystallizes with one molecule of water, forming thin needles (m.p. 237°). Caffeine has a somewhat bitter taste; it dissolves readily in hot water and has the effect of a stimulant on the nervous system.

Theobromine (3,7-dimethylxanthine) occurs in the cocoa bean (*Theobroma cacao*). It is a crystalline substance (m.p. 351°) with a poor solubility in water. Medicinally it is used as a diuretic.

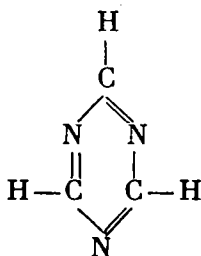
Adenine $C_5H_5N_5$, or 6-aminopurine, and *guanine* $C_5H_5ON_5$, or 2-amino-6-hydroxypurine, are the most widely distributed substances of the purine series:



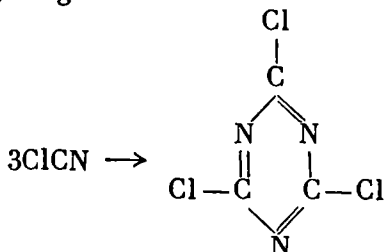
Adenine, as well as xanthine, hypoxanthine, and guanine, is a product of the hydrolysis of nucleic acids. These substances are very important biologically, as they are constituents of the cell nuclei. They occur in many plants: in tea, sugar-beets, hops, etc. Large quan-

tities of them are also contained in yeast, in animal tissues, as well as in urine and guano. A considerable amount of guanine is found in the scales and skin of fish, reptiles, and amphibians; in fact, it is this substance that is responsible for the peculiar metallic lustre of their scales. Adenine is a crystalline substance; it melts at about 360° and has rather pronounced basic properties. Guanine is insoluble in water; with acids it forms salts, which are hydrolyzed to a high degree.

324. Triazine. Cyanuric Chloride. Selective Herbicides. The most important of the heterocyclic compounds with three nitrogen atoms in the ring is the six-membered heterocyclic compound symmetric triazine:

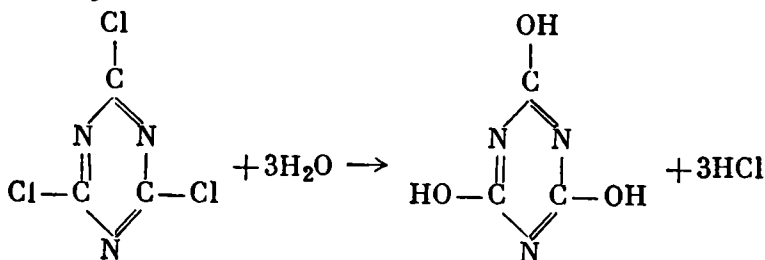


Its most important derivative cyanuric chloride, is prepared by polymerizing *chlorocyanogen*:



The process is conducted in the gas phase at $350\text{--}400^{\circ}$ over a catalyst: activated charcoal impregnated with chlorides of metals.

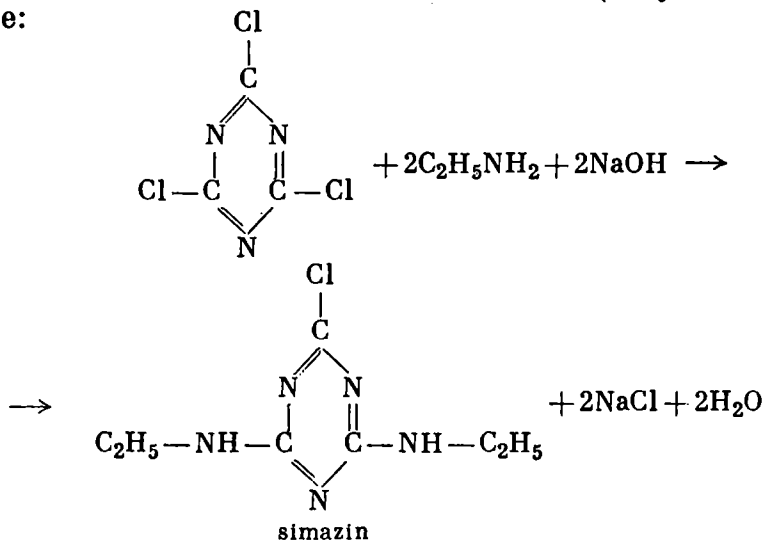
Pure cyanuric chloride is a white crystalline substance, which melts at $146\text{--}147^{\circ}$. It is slightly soluble in water, but dissolves well in most organic solvents. The chlorine atoms in the cyanuric chloride molecule are highly mobile and can relatively easily be replaced with other groups. One, two, or three chlorine atoms can be replaced. Treatment with water—especially easily by boiling—brings about the substitution of hydroxyl groups for the chlorine atoms, with the formation of *cyanuric acid*:



The reaction with alcohols or phenols proceeds similarly, with the formation of corresponding esters.

Many cyanuric chloride derivatives have important applications in various fields of organic chemistry.

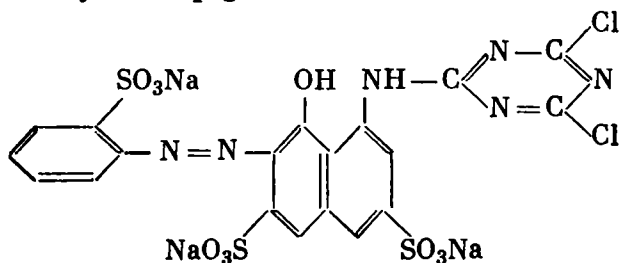
The treatment of cyanuric chloride with ethylamine in an alkaline medium (with slight heating) causes the replacement of two chlorine atoms and the formation of 2-chloro-4,6-bis-(ethylamino)-symmetric triazine:



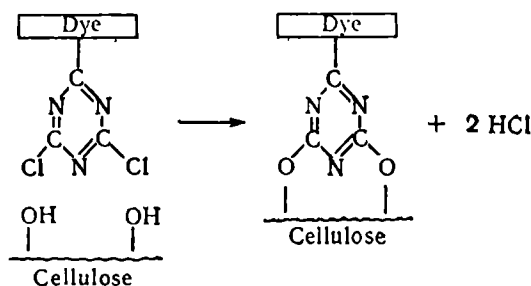
Under the commercial name of *simazin* this compound is used extensively in farming as a selective herbicide for maize crops. It effectively controls weeds, while having no detrimental effect on the main crop.

325. Active Pigments. Optical Bleaching Agents. In the past 20 years chemists have synthesized particularly fast dyes, known as *active pigments*, which form a chemical (covalent) bond with fibres of a vegetable origin (cotton and viscose).

Their preparation begins with a reaction between cyanuric chloride and some compound that already has a chromophore group, an auxochrome group, and an acid group (for solubility). It is customary to use for this purpose dyes with a bright, beautiful colour, but not used as such because of their insufficient stability. The reaction with cyanuric chloride produces a dye incorporating the triazine ring with one or two mobile chlorine atoms. One compound of this type is the active yellow pigment:



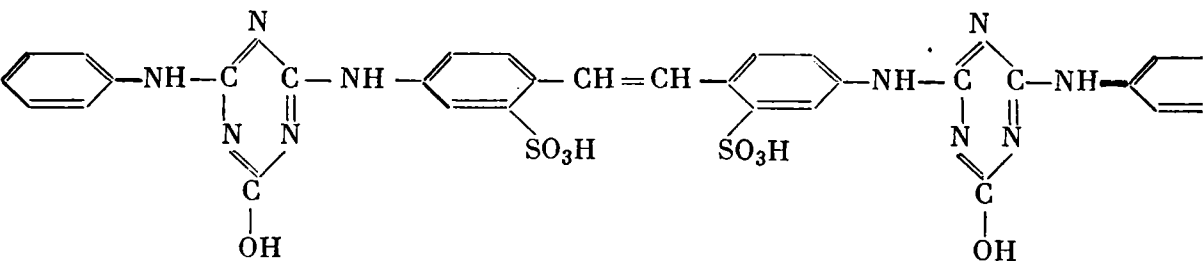
Such a dye can react chemically with the hydroxyl groups of cellulose. In its general form the formation of a colour on cellulose fibre by an active pigment can be represented as follows:



It was later established that, besides the triazine ring, certain other groups (such as the hydroxyethylsulphonic and the pyrimidon groups) can be used as linkages between the dye molecule and cellulose.

A great advantage of active pigments is their high degree of fastness and the possibilities they offer of obtaining very bright, light colours.

Cyanuric chloride is also used to prepare so-called *optical bleaching agents*, or *white dyes*. Their action is based on the phenomenon of fluorescence, the absorption of part of the invisible rays of the solar spectrum (ultraviolet) and their transformation into visible rays of a big wavelength (blue or violet). Since in most cases the ordinary impurities in textiles, paper, and synthetic detergents give these materials an undesirable yellowish or dirty yellowish colour, the addition of a substance with a blue fluorescence levels out the colour of the material to a pure white. Many optical bleaching agents are now known, and they belong to various classes of organic compounds. One of the most widespread is a derivative of cyanuric chloride with the following structure:

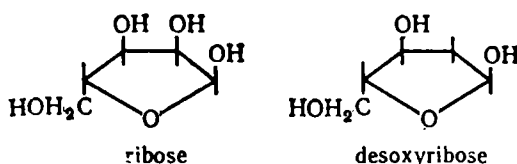


326. Nucleic Acids and Nucleotides. RNA and DNA. As was pointed out above (p. 359), all living cells and viruses contain *nucleoproteins*, compounds consisting of nucleic acids (NA) and proteins. The *nucleic acids*, or polynucleotides, are the principal components of cell nuclei

and are very complex high-molecular compounds. Research by chemists, biologists, and physicists has shown that polynucleotides consist of a large number of mononucleotide residues. The molecular weight of NA runs to several tens of millions.

It is now known that nucleic acids participate in several extremely important life processes.

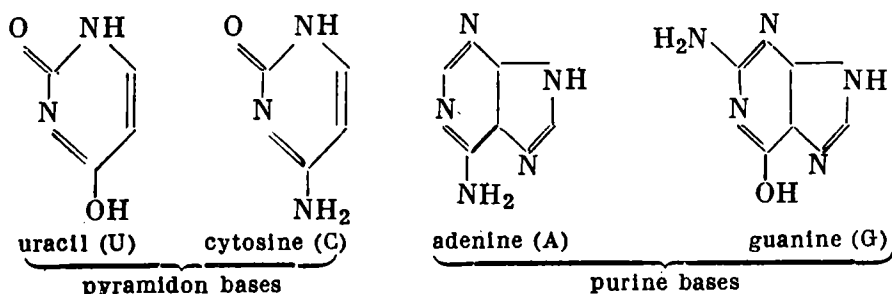
Two types of NA are distinguished: the *ribonucleic acids* (RNA) and the *deoxyribonucleic acids* (DNA). The two nucleic acids are similar in chemical nature and contain the carbohydrate pentose (p. 304). The RNA molecule contains ribose, while the DNA molecule contains desoxyribose, which differs from ribose in that it has fewer hydroxyl groups:



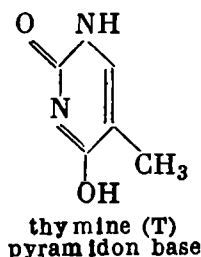
DNA constitutes the basis of the chromosomes and plays a direct part in the transmission of hereditary features. RNA participates in protein synthesis. Inside the cells the DNA and RNA are linked to proteins by loose bonds, which are in all probability of a salt-like character.

The hydrolysis of RNA and DNA by acids or enzymes has revealed that they contain four heterocyclic bases.

RNA contains the pyrimidin bases *uracil* (U) and *cytosine* (C) and the purine bases *adenine* (A) and *guanine* (G):

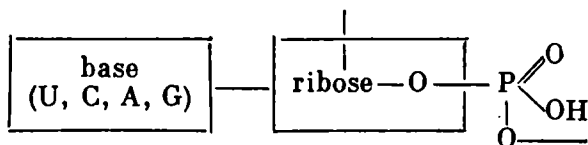


In DNA there is no uracil, but instead there is its homologue *thymine* (T):

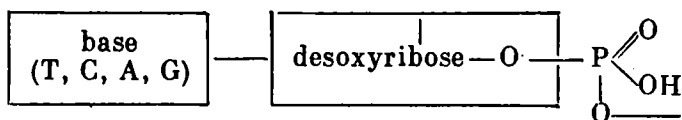


The mononucleotides inside the NA polymer molecule are linked by phosphoric acid radicals.

The monomer unit of the RNA polymer chain can be represented thus:



The monomer unit of DNA can be represented thus:



The DNA chain has the following structure:

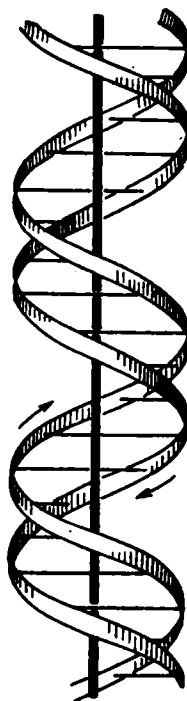
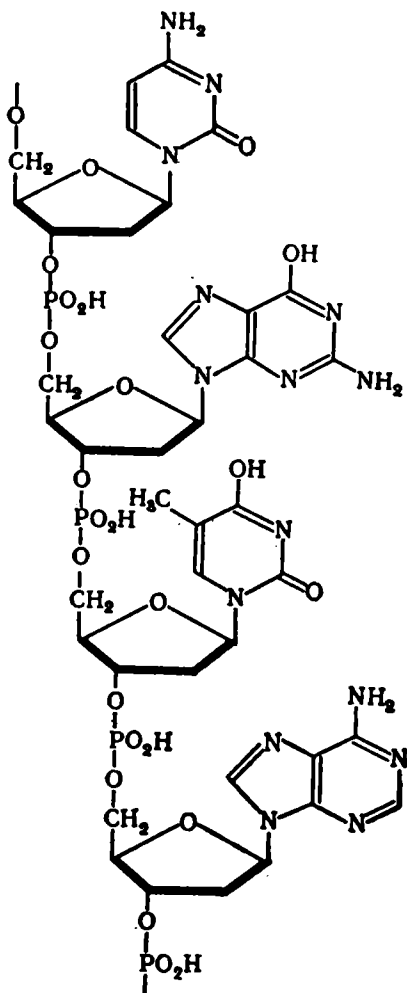


Fig. 79. Model of DNA molecule.

Although the DNA and RNA chains contain only four different bases, their molecular weight, running to several tens of millions, is so enormous that there can be an extremely large number of combinations of the various individual nucleic acids, combinations differing in the pattern and sequence of these bases.

X-ray analysis has revealed the structure of RNA and DNA, the type of linkage between the monomer units, their sequence, the character of the terminal groups, and the configuration and conformation of these macromolecules. It was established that the DNA molecules are twin polymer chains running parallel to each other along a spiral (Fig. 79).

The heterocyclic bases of these two parallel helices are directed into the interior of the spiral and are linked in pairs by intermolecular hydrogen bonds. It has been found that these hydrogen bonds can arise only between pairs of quite definite bases, for example, A and T, G and C.

The RNA conformation differs sharply from the DNA conformation. RNA is a single—and not double—thread. Depending upon external conditions, it can be either a tangled skein, or a rod, or a stretched out thread.

An impressive hypothesis has now been built up about the parts that DNA and RNA play in protein synthesis and in heredity.

The nucleic acids, together with proteins, are thus the vehicles of most important biological functions and determine all the characteristics that distinguish living from non-living matter, namely metabolism, the ability to respond to environmental changes, and reproduction.

Conclusion

In conclusion, it seems appropriate to consider once again the role of the theory of chemical structure in the study of organic chemistry.

Engendered, like every other science, by the practical requirements of production, organic chemistry some 150 years ago became a branch of chemistry in its own right, a branch concerned at first with the transformations and properties of substances produced in living organisms.

The first successful attempts to approach the chemistry of the natural carbon compounds from scientific positions involved the most readily available compounds of the simplest structure. The objects of investigation were fatty acids, alcohols, and hydrocarbons. The study of the characteristic features of these substances led to the synthesis of compounds that do not occur in nature: acid chlorides, halogen derivatives of hydrocarbons, diazo-compounds, and many others. Industrial progress in the first half of the past century and the extension of the field of application of various organic substances of natural origin (dyes, tanning matter, etc.) considerably stimulated interest in organic chemistry and specialized research. Experimental findings, for their part, called for theoretical summarizing that would account for the diversity of organic substances and the various phenomena observed in their transformations.

Butlerov's profoundly materialistic and essentially dialectical theory of chemical structure, which came into being in the latter half of the past century, elevated organic chemistry to a new and higher plane. This theory not only explained the experimental data that had accumulated, but also made it possible to predict new facts and new compounds, as well as rationally to choose ways of synthesizing these compounds. The fundamental principles of the theory of chemical structure exerted a lasting influence on the basic trends in the development of organic chemistry and are its mainstay.

Enriched in the course of its development with new facts and concepts drawn from stereochemistry, chemical kinetics, and other sections of chemistry, the theory of chemical structure provides a key to learning the structure and properties of complicated organic molecules and makes it possible to approach the most involved problems of organic chemistry strictly scientifically.

It is highly important for the organic chemist to be familiar with the techniques of individualizing and identifying organic compounds. But it is even more important for him to have a deep understanding of the structural formula of a compound; he must be able to visualize, on the basis of that structural formula, the physical and chemical properties of the compound in question. For example, the presence of a carboxyl or amino group in the molecule is an indication that the substance has acid or basic properties respectively, while a large weight of the hydrocarbon part of the molecule points to a low solubility of the substance in water and a considerable solubility in organic solvents. The opposite inference can be drawn from the presence of a large number of hydroxyl or sulphonyl groups. Often the structural formula of a compound throws light on such properties as readiness to undergo oxidation or ability to experience hydrolytic decomposition. The presence of characteristic "chromophore" groups (azo-group, quinoid system, etc.) indicates that a compound has colour.

At the same time it should not be forgotten that, while reflecting the actual structure of a molecule, a structural formula (as written conventionally) is merely a schematic representation of the molecule and fails to take into consideration several factors affecting the molecule's properties. The most important of these factors are the spatial distribution of the atoms in the molecule and the mutual influence of the various parts of the molecule. The ability to "read" structural formulas correctly should therefore be based not on memorizing various general principles formulated in the course, but on a thorough knowledge of the factual material of modern organic chemistry. Such a knowledge does not come at once, nor is it acquired by merely committing to memory a multitude of facts; it is a result, rather, of an understanding of the general scheme, system, and methods of organic chemistry.

A first reading will by no means always produce a clear understanding, let alone assimilation of the factual material.

In the concluding lines of his famous *Introduction to a Comprehensive Study of Organic Chemistry*, Bulterov wrote:

"May the *future chemist* studying this book permit me to conclude it with a word of advice: on reading it, to start from the beginning once more. What he was able to glean from a careful reading of the book to the end will suffice to enable him, on reading it a second time, to get a much clearer picture of many things, to form his own, critical views on many points, and, without taking anything he has read for granted, to assess, on the one hand, the mutual relationships of various factors and considerations, and, on the other hand, their merits and faults."

I. Nomenclature of Organic Compounds

In order to be able to use handbooks efficiently and fully comprehend the chemical literature, one must have a good understanding of the names of chemical compounds, i.e., have a firm command of the chemical nomenclature. A study of the nomenclature is also useful since it helps to grasp the system of classifying chemical compounds and the structural relationships between compounds of different classes.

For a nomenclature really to serve as the common language of chemists, it must describe the chemical structure of compounds and provide a strict correspondence between the names of molecules and their structure. Such a nomenclature is called *structural*. The present-day structural nomenclature is actually a nomenclature not of substances, but of structural formulas.

The first structural nomenclature was the so-called "old rational nomenclature", which is in use to this day. However, progress in organic synthesis made it clear even in the last decade of the past century that, as logical and simple as it was, the rational nomenclature was becoming inadequate. Newly synthesized complex compounds could no longer adequate for naming complicated organic compounds.

In 1892 a special international congress of chemists at Geneva approved the basic principles and rules of a new official international nomenclature, which came to be known as the *Geneva* nomenclature. Very logical and closely related to the scientific classification of organic compounds, the Geneva nomenclature was elaborated particularly for compounds in which all the carbon atoms are linked directly with one another and not via some heteroatom, primarily for open-chain carbon compounds. It did not provide names for certain types of complex polyfunctional, organoelement, and various cyclic compounds. Therefore, the major handbooks and journals of abstracts introduced their own supplements to the official nomenclature, supplements at times of an arbitrary nature.

The nomenclature closest to the Geneva system is that adopted in the 4th edition of *Beilstein's Handbuch der Organischen Chemie*, founded by the Russian scientist F. Beilstein.

The work of unifying the nomenclature, undertaken by the International Union of Pure and Applied Chemistry (IUPAC), resulted in the adoption, in 1930, of a new set of rules, known as the *Liege* rules. The Liege system, various versions of which became widespread in the chemical literature, countenanced several names for a compound, unlike the Geneva system, which permitted only one name. Not satisfied with the Liege system, the major handbooks and periodicals followed nomenclature versions of their own.

Such a state of affairs required a new revision of the nomenclature, which was begun in the fifties and continues to this day. A conference in Paris in 1957 adopted rules for the nomenclature of hydrocarbons and cyclic structures. These are known as the "IUPAC 1957 Rules". In 1962 IUPAC published for discussion a nomenclature of compounds with substituents other than carbon, compounds containing the halogens, O, N, S, Se, or Te.

Big advances in highly specialized departments of chemistry (the chemistry of the steroids, hydrocarbons, amino acids and peptides, nucleic acids, etc.) gave rise to "localized" nomenclatures adapted to certain small regions of chemistry. This is an asset for the specialist, but defies comprehension by the non-specialist.

Chemistry is indivisible, and, in addition to regional dialects, it must also have a common official language. Chemists require a structural nomenclature that would be simple, unambiguous, consistent, and free from internal contradictions. None of the existing systems fully satisfies these requirements. They have to be satisfied by a truly systematic nomenclature.

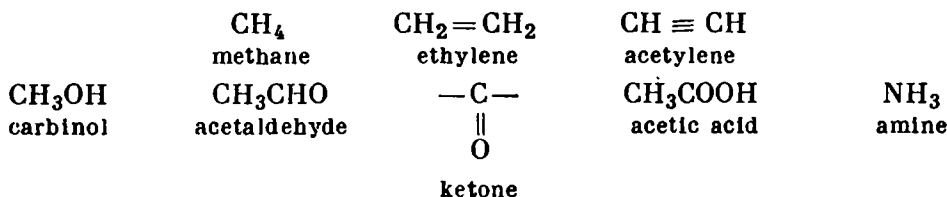
At the present time there is no uniformity of nomenclature in the chemical literature of the world. Various publications use the old rational nomenclature, the Geneva system, the Liege system, and the new IUPAC official nomenclature, which has not yet been completed.

The main types of nomenclature in use are described below.

The principles of the Geneva nomenclature, the most logical of them all, are described in detail, since all the subsequent systems have used the same means of expression.

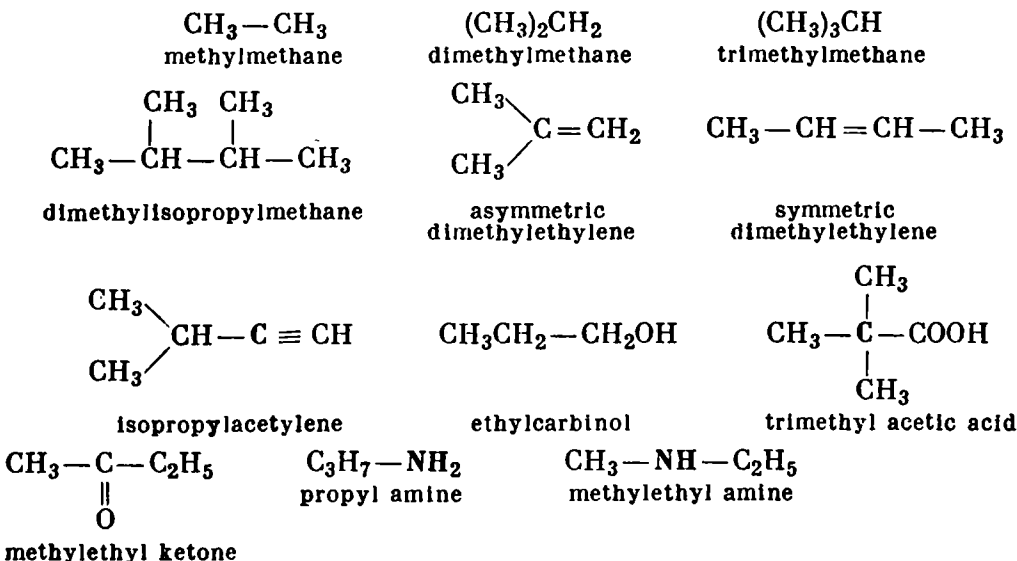
1. THE "RATIONAL" NOMENCLATURE

The "rational" name of a compound is based on the name of some simple "nucleus" of a molecule:



Names are formed by adding the names of radicals to the name of such a "nucleus".

For example:



2. THE GENEVA NOMENCLATURE

The principles of the Geneva nomenclature, as adopted in Beilstein's *Handbuch* are set forth below. The logical nature of this and its close relationship with the scientific classification of organic compounds reduce the scope for the introduction of arbitrary names.

This nomenclature has been worked out most thoroughly for what Butlerov called "integral" compounds, i.e., compounds in which all the carbon atoms are linked directly with one another. In such compounds there are only pure (unsubstituted) functional groups (OH, NH₂, ...).

The naming of such compounds follows a single simple pattern (see p. 591). The compound's name is a compound word consisting of a root (main chain) and prefixes and suffixes (functional and other groups). Each element of the name has a definite place in the compound word. The diagram shows how the name of a compound depends on the scientific classification of organic compounds. In the preceding chapters we have seen repeatedly that an understanding of these rules and their applications enables the student to remember the nomenclature and derive satisfaction from exercises in it.

GENERAL PRINCIPLES

The names of compounds under the Geneva system are determined by:

1. the structure of the principal skeleton of the compound;
 2. the character and number of the substituent groups, with due consideration for their "seniority", and
 3. the principle of maximum simplicity, other conditions being equal.
- In structure of principal skeleton, organic compounds are divided into:
- (a) acyclic systems,
 - (b) carbo-, or isocyclic, systems, and
 - (c) heterocyclic systems.

The names of substances in the Geneva nomenclature follow the ordinary grammatical principles of word-forming. The "root" of the word is the name of the longest unbroken chain of carbon atoms, which corresponds to some hydrocarbon. Formally, by replacing hydrogen atoms in such a hydrocarbon by functional groups and other substituents in a strictly definite order, we can arrive at the full name of the compound.

For every functional or non-functional substituent there are quite definite names and places either before or after the name of the principal chain.

The names of the main compounds (hydrocarbons, alcohols, primary amines, etc.) usually consist of one word; derivatives of the main compounds (ethers, esters, acid chlorides, amides, etc.) are denoted by several words. The complexity of the name is determined by the complexity of the compound's structure.

To give a compound its official name it is first of all necessary to identify the longest carbon atom chain in it.

Hydrocarbon radicals enjoy the highest seniority in numbering the principal chain. The position of two radicals being equal, the one with fewer carbon atoms is the senior. The name of the radical is derived from the name of the hydrocarbon with the same number of carbon atoms, the suffix *yl* being substituted for the suffix *ane*.

If the radical contains multiple bonds, i.e., corresponds to an unsaturated hydrocarbon (whose names end in *ene* or *yne*), the suffix is not dropped, but a second, *yl*, is added.

The names of radicals precede the name of the principal chain. A figure with a hyphen before the radical shows to which carbon atom of the principal chain it is attached.

Multiple bonds are denoted by the suffix *ene* (double bond) or *yne* (triple bond), which replace the suffix *ane*, corresponding to the saturated hydrocarbon.

Multiple bonds come second in seniority, i.e., they determine where numbering begins if it is not determined by branchings of the chain. The triple bond is higher in seniority than the double bond.

Functional groups* containing oxygen or sulphur come next (third) in seniority. The designations corresponding to these groups are attached to the word at the end.

If a compound contains two or more long chains with the same number of carbon atoms, the most complex one is chosen, i.e., the one with the most branches or substituents.

Once the principal chain is chosen, the initial point of the numbering has to be determined; this is done on the basis of the substituents in the principal chain and their seniority.

The substituents are divided into hydrocarbon radicals, functional and non-functional groups. Besides this, the multiple (double and triple) carbon-carbon bonds are taken into account and designated in the name, as if they too were substituents.

Nitrogen-containing functional groups come next in seniority, occupying a lower position. The designations of these groups are added to names of compounds before the names of the hydrocarbon radicals, i.e., in the form of prefixes.

Non-functional groups come last in seniority, i.e., they determine the initial point of the numbering only if there are none of the previous substituents or if these are symmetrically situated. Non-functional groups are designated at the very beginning of the names of compounds.

Functional Groups Containing Oxygen or Sulphur (in order of rising seniority)

Formula	Name	Formula	Name
—OH	ol-	$\begin{array}{c} \text{O} \\ \diagup \\ \text{—[C]} \\ \diagdown \\ \text{OH} \end{array}$	oic acid
—SH	thiol-	$\begin{array}{c} \text{S} \\ \diagup \\ \text{—[C]} \\ \diagdown \\ \text{OH} \end{array}$	thionic acid
$> \text{[C]} = \text{O}$	one-	$\begin{array}{c} \text{S} \\ \diagup \\ \text{—[C]} \\ \diagdown \\ \text{SH} \end{array}$	thiolthionic acid
$> \text{[C]} = \text{S}$	thione-	—SO ₂ H	sulphinic acid
$\begin{array}{c} \text{O} \\ \diagup \\ \text{—[C]} \\ \diagdown \\ \text{H} \end{array}$	al-	—SO ₃ H	sulphonic acid
$\begin{array}{c} \text{S} \\ \diagup \\ \text{—[C]} \\ \diagdown \\ \text{H} \end{array}$	thial-		

* Functional groups are groups of atoms containing the [C]—A—H unit, where A is an atom or group of atoms of oxygen, sulphur, or nitrogen (but not carbon). The carbonyl is also regarded as such a group.

Nitrogen-Containing Functional Groups
(in order of rising seniority)

Formula	Name
—NH ₂	-amino
—NHOH	-hydroxylamino
—NH—NH ₂	-hydrazino
etc.	

Non-Functional Groups
(in order of rising seniority)

Formula	Name	Formula	Name
—F	-fluoro	—NO	-nitroso
—Cl	-chloro	—NO ₂	-nitro
—Br	-bromo	—N ₃	-azido
—I	-iodo		

The application of the basic principles of the Geneva nomenclature will best be illustrated by the nomenclature of the simplest organic substances: hydrocarbons with an open chain of carbon atoms. Below we shall consider how the names of acyclic compounds with various substituents are composed.

The nomenclature of the carbocyclic and heterocyclic compounds involves several additional rules, but in the main follows the principles and rules formulated for acyclic systems.

A general diagram of the elements that make up the name of a complicated compound is given on p. 591.

ACYCLIC HYDROCARBONS

Saturated Hydrocarbons of Normal Structure (Alkanes, Paraffins)

SECTION ONE

1. The names of saturated hydrocarbons have the suffix *ane*. The first four hydrocarbons have historical names; the names of the rest are based on the Greek numerals corresponding to the number of carbon atoms.

2. The straight-chain hydrocarbons have the following names:

Formula	Name	Formula	Name
CH_4	Methane	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	Tetradecane
CH_3CH_3	Ethane	$\text{CH}_3(\text{CH}_2)_{13}\text{CH}_3$	Pentadecane
$\text{CH}_3\text{CH}_2\text{CH}_3$	Propane	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$	Hexadecane
$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	Butane	$\text{CH}_3(\text{CH}_2)_{15}\text{CH}_3$	Heptadecane
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	Pentane	$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$	Octadecane
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	Hexane	$\text{CH}_3(\text{CH}_2)_{17}\text{CH}_3$	Nonadecane
$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	Heptane	$\text{CH}_3(\text{CH}_2)_{18}\text{CH}_3$	Eicosane
$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	Octane	$\text{CH}_3(\text{CH}_2)_{19}\text{CH}_3$	Heneicosane
$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$	Nonane	$\text{CH}_3(\text{CH}_2)_{20}\text{CH}_3$	Docosane
$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	Decane	$\text{CH}_3(\text{CH}_2)_{28}\text{CH}_3$	Triacontane
$\text{CH}_3(\text{CH}_2)_9\text{CH}_3$	Undecane	$\text{CH}_3(\text{CH}_2)_{38}\text{CH}_3$	Tetracontane
$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	Dodecane	$\text{CH}_3(\text{CH}_2)_{48}\text{CH}_3$	Pentacontane
$\text{CH}_3(\text{CH}_2)_{11}\text{CH}_3$	Tridecane	$\text{CH}_3(\text{CH}_2)_{58}\text{CH}_3$	Hexacontane
			etc.

Saturated Hydrocarbons with Branched Chains (Isoalkanes)

SECTION TWO

The names of the isoalkanes are composed as follows:

- I. The name of the principal chain is indicated.
- II. The alkyl name is written before the name of the principal chain
- III. The name has the ending *ane*.

II	I	III
alkyls	principal chain	ending <i>ane</i>

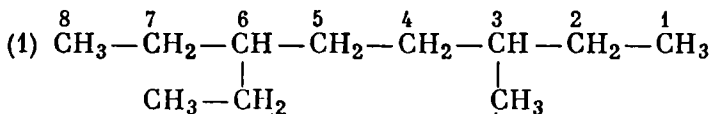
3. The name of the compound has as its basis (word root) the name of the hydrocarbon corresponding to the number of carbon atoms in the principal chain. The principal chain is:

- (a) the longest chain,
- (b) the most complicated chain.

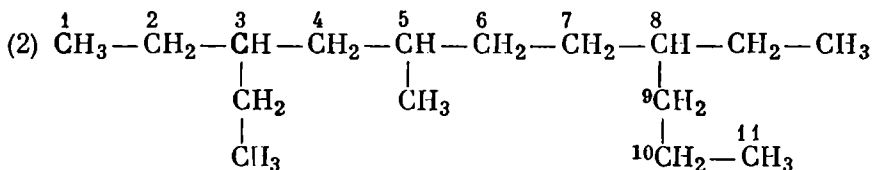
If a compound has two or more equally long chains, the one with the most branches is regarded as the principal one.

4. When the principal chain has been found it is necessary to number the carbon atoms. The numbering runs from the end of the chain to which one of the alkyls is closest. If different alkyls are in equal positions in relation to the ends of the chain, preference is given to the end where the radical has fewer carbon atoms (methyl, ethyl, propyl, etc.).

Examples:



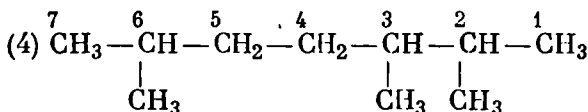
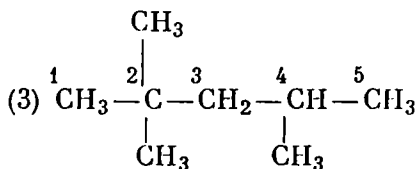
the methyl radical determines the end where the numbering begins



the ethyl radical determines the end where the numbering begins.

If identical radicals are at equal distances from the chain ends, the chain is numbered from the end where there are more branches.

Examples:



5. Once the principal chain has been identified and its carbon atoms numbered, it is possible to set about writing the name of the compound. The simplest substituents are indicated first: methyl or, in its absence, ethyl, etc. A figure indicating the number of the carbon atom (in the principal chain) to which the radical is attached is written before the radical. The figure is separated from the name of the radical by a hyphen. Following the methyl radical, it is necessary to name the ethyl radical, and so on in the order of mounting carbon atoms in the radical, following which the hydrocarbon corresponding to the principal chain of carbon atoms is named.

If the hydrocarbon contains several identical radicals, their number is written out before the name of the radicals; all the numbers of these radicals are designated by figures. The figures are set off by commas, arranged in mounting order, and put before the name of the radicals.

The hydrocarbons whose formulas are given above should, accordingly, be named as follows:

- (1) 3-methyl-6-ethyloctane;
- (2) 5-methyl-3,8-diethylenedecane;
- (3) 2,2,4-trimethylpentane;
- (4) 2,3,6-trimethylheptane.

Unsaturated Hydrocarbons (Alkenes, Alkynes)

SECTION THREE

6. The names of unsaturated hydrocarbons are composed according to the scheme:

II	I	III
alkyls	principal chain	multiple bonds

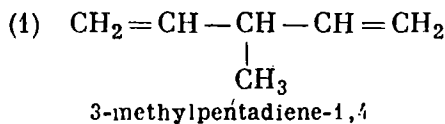
7. The numbering is determined by the alkyls of the principal chain, as in the case of saturated hydrocarbons. In the absence of alkyls, the numbering is determined by the multiple bond closest to the chain end. If a double and a triple bond are in identical positions in relation to the ends of the chain, the triple bond is regarded as the senior, and the numbering is done from that end.

8. The names of unsaturated hydrocarbons are formed from the names of saturated hydrocarbons with the same number of carbon atoms by substituting the suffix *ene* (for alkenes) or *yne* (for alkynes) for the suffix *ane* (of the alkane).

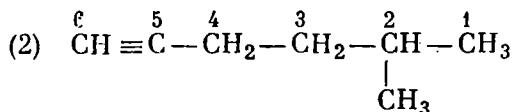
The position of each multiple bond in the principal chain is denoted by a figure following the suffix and separated from it by a hyphen. The figure corresponds to the number of one of the multiply bound atoms (that whose number is lower).

9. A hydrocarbon with several multiple bonds has a complex ending in which the number of multiple bonds and their character are written out; the *ene* precedes *yne* regardless of the numbering.

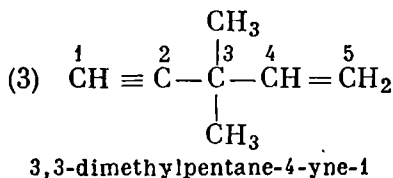
Examples:



order of numbering optional



numbering determined by side chain



double bond and triple bond at equal distances from chain ends; numbering determined by triple bond.

**Compounds with Oxygen-Containing Functional Groups
(Alcohols, Aldehydes, Ketones, Acids)
and Their Sulphurous Analogues**

SECTION FOUR

10. The principal chain is identified in the same way as above. The numbering is determined above all by alkyls and, following that, by multiple bonds. Should they be absent or symmetrically situated, the order of numbering is determined by oxygen-containing functional groups, preference going to the group which:

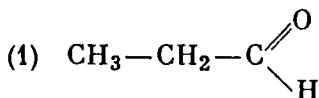
- (a) is situated closer to one of the ends of the chain,
- (b) is the senior one in the section.

The seniority of the groups is determined by the greater degree of oxidation, a functional group containing sulphur enjoying seniority over a corresponding oxygen-containing group.

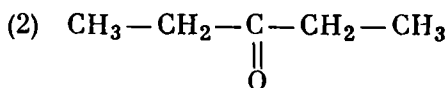
11. The names of these groups are designated by endings which come after the name of the principal chain and follow the designations of the multiple bonds. The carbon of the functional groups is accounted for in the principal chain. Its number follows the name of the group. In sulphurous analogues it is the number of the carbon atom linked directly to the sulphur atom.

The designations of oxygen- or sulphur-containing functional groups and their order of seniority are given on p. 583.

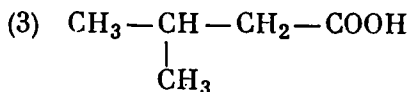
Examples:



propanal



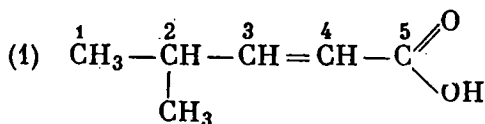
pentanone-3



2-methylbutanoic-4 acid

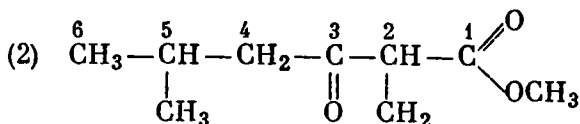
12. If a compound contains several functional groups, their designations follow one another in the order of mounting seniority.

Examples:



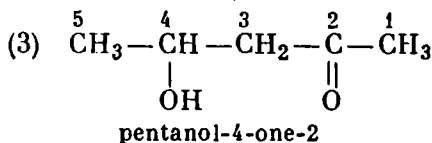
2-methylpentene-3-oic-5 acid

numbering begins from radical closest to end (methyl)



2,5-dimethylhexanone-3-oic-1 methylate

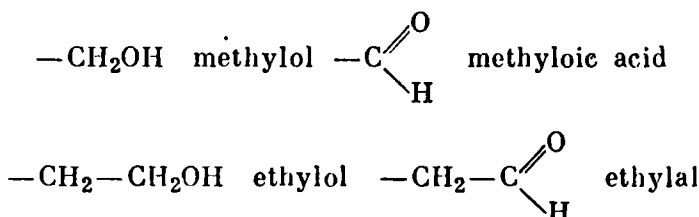
order of numbering determined by COOCH_3 group



order of numbering determined by seniority of keto group.

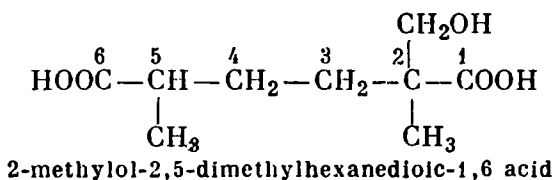
13. If the oxygen-containing functional groups are in the side chains (alkyls), their names are incorporated in the names of the same alkyl groups.

Example:



14. Should the alkyls determining the order of numbering be in equal positions, priority is given to oxygen-containing (complex) alkyls.

Example:



order of numbering determined by oxygen-containing methyl group.

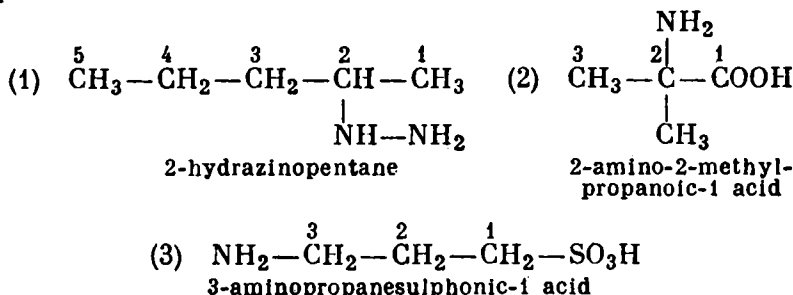
Nitrogen-Containing Functional Groups

SECTION FIVE

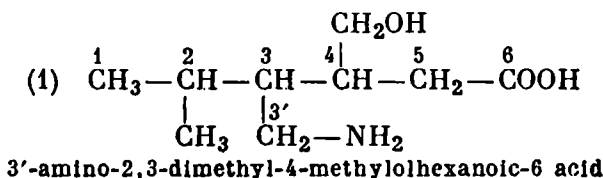
15. The principal representatives of this section are given in the order of mounting seniority (for order of numbering) in the table on p. 584.

These substituents determine the order of numbering in the principal chain in the absence of representatives of sections 2, 3, and 4.

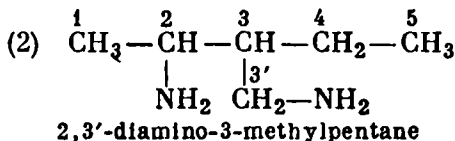
The name of these substituents precedes the name of the radicals. An amino group is named first, then a hydroxylamine group, and, finally, a hydrazino group. The figure designating the number of the carbon atom (in the principal chain) to which the substituent is attached is put in front and separated by a hyphen.

Examples:

16. If the amino group is in the side chain, its name is placed before the names of the radicals, indicating the number of the carbon atom (in the side chain) to which the amino group is attached.

Examples:

skeleton is not symmetric; order of numbering is determined by the methyl group



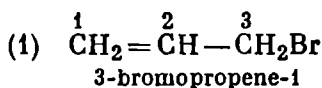
Non-Functional Substituents

SECTION SIX

17. Seven non-functional substituents are known; they do not contain hydrogen atoms and are arranged in mounting seniority according to the table on p. 584.

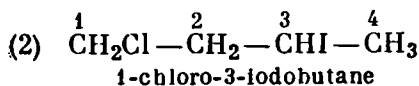
In their effect on the order of numbering the non-functional substituents come last, i.e., they determine the order of numbering only provided it has not been determined by substituents of either the second, or the third, or the fourth, or the fifth section.

18. If, however, the order of numbering is determined by non-functional substituents, preference is given to the one closest to an end of the principal chain. In the event of equal positions, priority is given to the senior substituent.

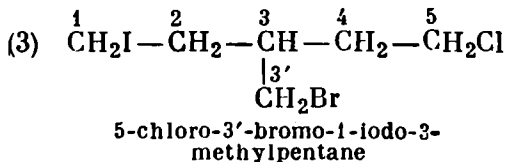
Examples:

order of numbering determined by multiple bond

[illegible]



order of numbering determined by substituent closest to end



order of numbering determined by senior substituent.

19. The names of substituents of section six are placed before the names of all other substituents. A figure separated by a hyphen indicates the number of the carbon atom (in the principal or the side chain) to which the substituent is attached. The order in which substituents of the sixth section are named is in reverse to their seniority in determining the order of numbering.

In the foregoing we have considered the rules for forming the names of organic acyclic compounds. The principal chain is identified according to the number of carbon atoms and the complexity of the chain, while the order in which it is numbered is determined by the substituents present.

The effect which substituents have on the order of numbering depends upon the seniority of the sections (II-III-IV-V-VI) and upon the seniority of the groups in the sections. On the opposite page is the general diagram for forming the name of a complicated organic compound of the acyclic division.

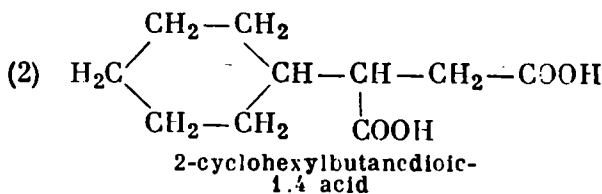
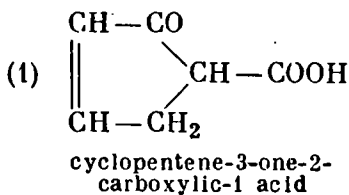
Carbocyclic Compounds

The main principles and rules of the official nomenclature with respect to acyclic compounds apply to carbocyclic compounds. A few distinctive features should, however, be noted.

20. The name of a monocyclic saturated hydrocarbon is based on the name of the corresponding normal hydrocarbon with the same number of carbon atoms, to which the prefix "cyclo" is added.

21. A carboxyl linked to the cycle is designated by the ending "carboxylic acid". If a side chain is long and complex, the substance is named as an acyclic substance, while the cycle, as any other substituent, is designated by a corresponding prefix, like a radical (e.g., cyclopentyl, cyclohexyl, etc.).

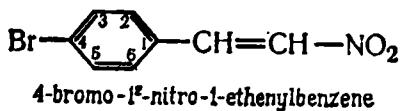
Examples:



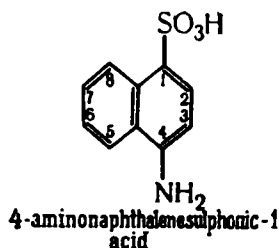
22. Aromatic compounds are usually named as derivatives of corresponding hydrocarbons.

Examples:

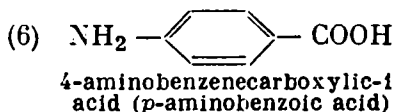
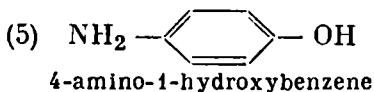
(3)



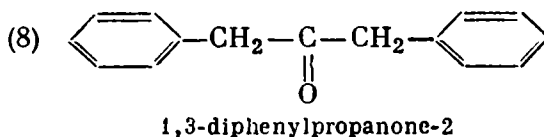
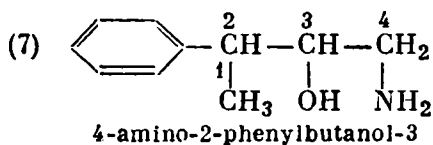
(4)



23. If a hydroxyl group is linked directly to the nucleus, it is designated by the prefix "hydroxy" before the name of the radicals (i.e., is transferred to section 5).

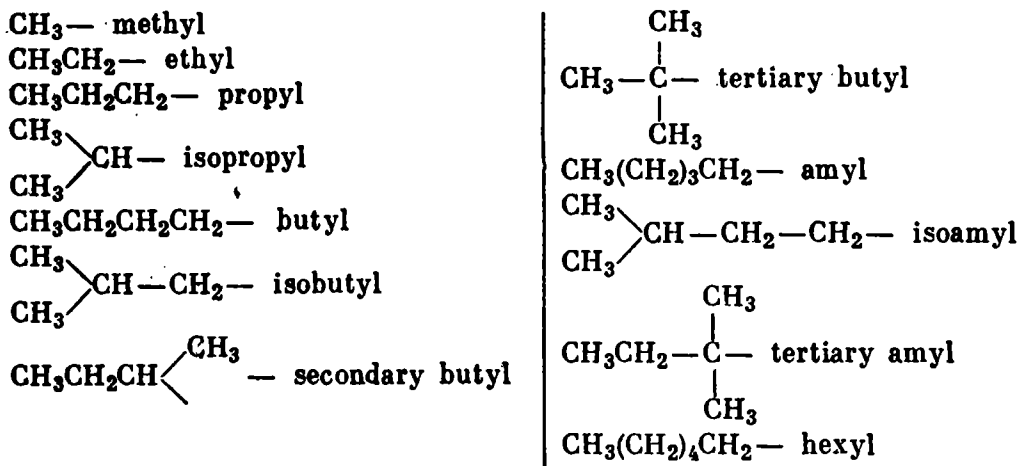
Examples:

24. If an aliphatic-aromatic compound has a long and branched side chain, the name of the compound is formed on the basis of the side chain, while the aromatic ring is treated as a substituent.

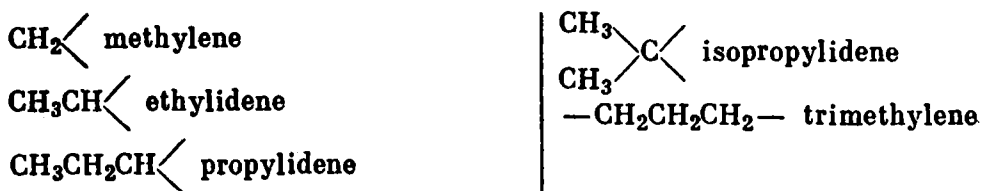
Examples:

II. Names of Common Radicals and Cyclic Structures

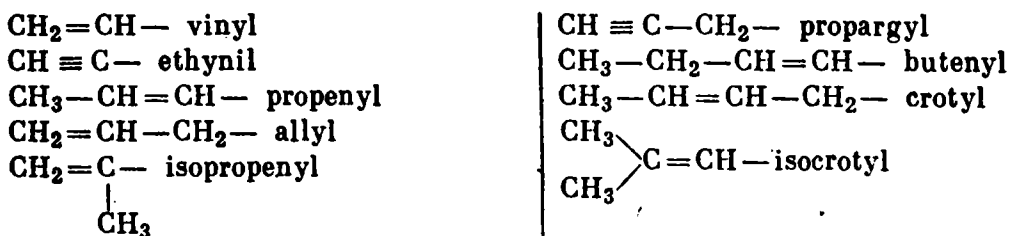
Monovalent Radicals of Saturated Hydrocarbons



Bivalent Radicals of Unsaturated Hydrocarbons



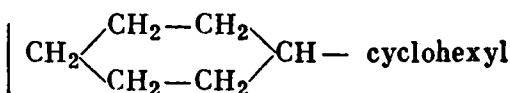
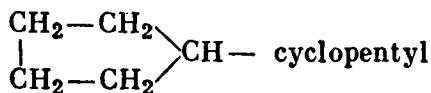
Radicals of Unsaturated Hydrocarbons



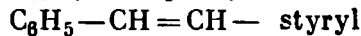
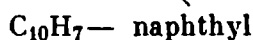
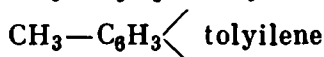
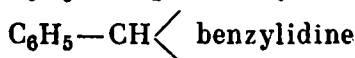
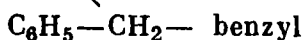
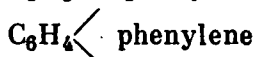
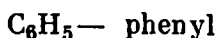
Bivalent Radicals of Unsaturated Hydrocarbons



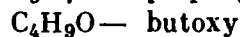
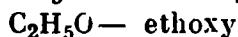
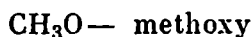
Alicyclic Hydrocarbon Radicals



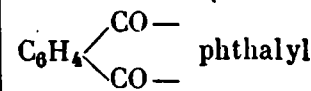
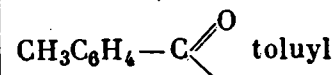
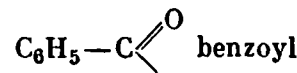
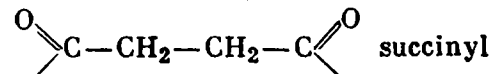
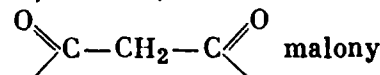
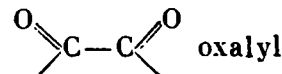
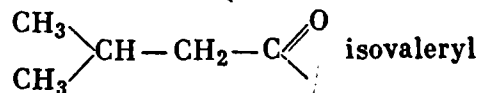
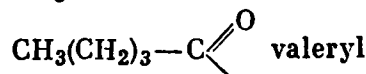
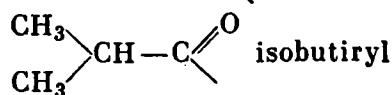
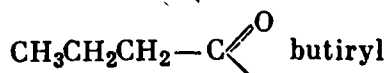
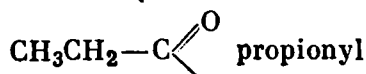
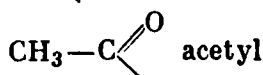
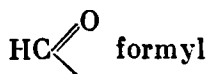
Aromatic Hydrocarbon Radicals



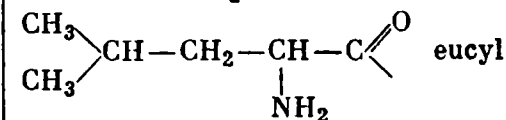
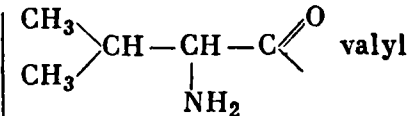
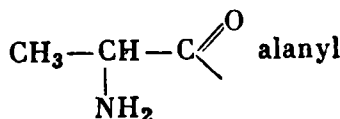
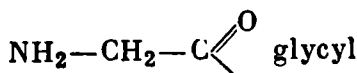
Alcohol Radicals

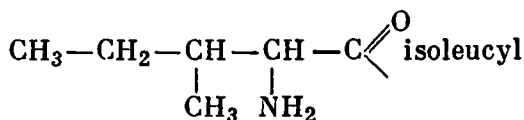
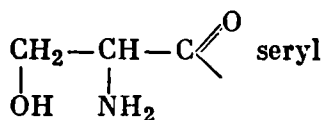


Acid Radicals

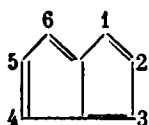


Amino Acid Radicals

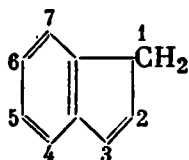




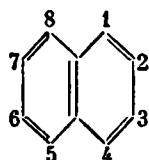
The Most Important Condensed Ring Carbocyclic Structures



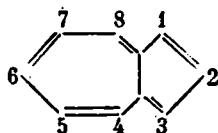
pentalene



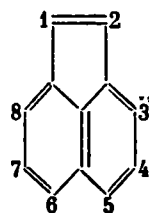
indene



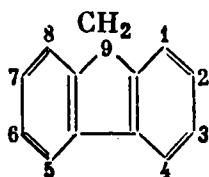
naphthalene



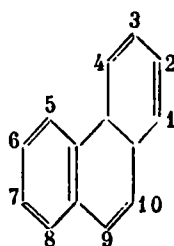
azulene



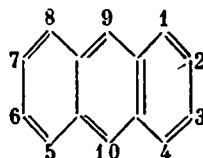
acenaphthylene



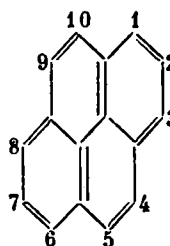
fluorene



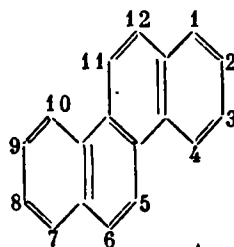
phenanthrene



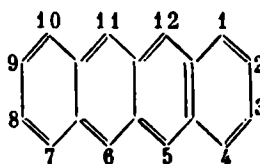
anthracene



pyrene

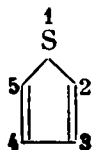


chrysene

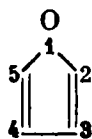


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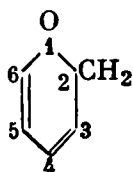
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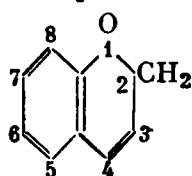
thiophene



furan



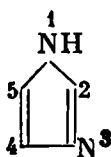
2H-pyran



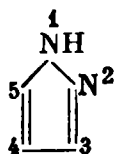
2H-chromene



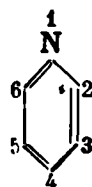
pyrrole



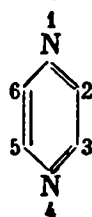
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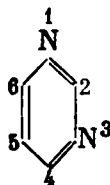
pyrazole



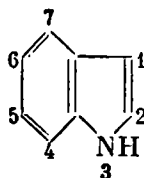
pyridine



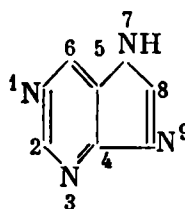
pyrazine



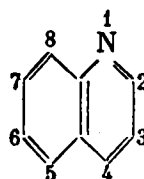
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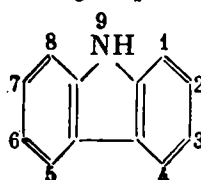
indole



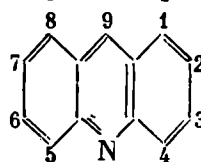
purine



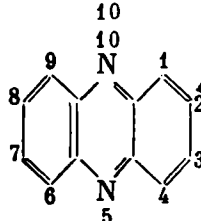
quinoline



carbazole

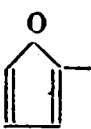
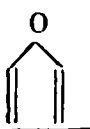
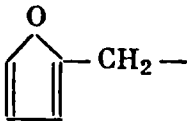
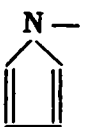
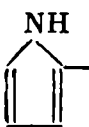
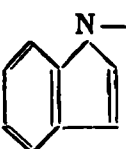
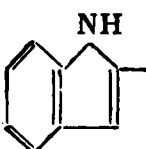
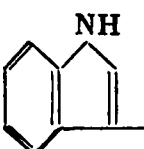


acridine



phenazine

Heterocyclic Compound Radicals

C_4H_3O-	furyl			
C_6H_5O-	furfuryl			
C_4H_4N-	pyrryl			
C_4H_3S-	thienyl			
C_5H_4N-	pyridyl			
C_8H_6N-	indolyl			

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